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INVESTIGATION OF THE COPRECIPITATION OF SULFIDES BY MEANS OF RADIOACTIVE INDICATORS

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The coprecipitation of various substances which, under the experimental conditions, should remain in solution, with analytical precipitates of low solubility is very common in chemical analysis.

Coprecipitation interferes with the preparation of pure precipitates of the correct stoichiometric composition, and also with complete separation of the elements, where it plays a negative part. This phenomenon has real significance, since it presents a possibility of separating traces of elements and also of studying the properties of elements at very high dilution.

The laws governing the processes of trapping easily-soluble compounds by a solid phase at the moment of their separation or formation have been studied by macro-, micro- and ultramicro- quantitative methods. In experiments on coprecipitation on the macro and micro-scales, normal analytical methods are used. When working on the ultramicro scale, where dilution can be of the order of 10^{-20} mol/liter, the methods already indicated are not suitable. In order to investigate the properties of such small amounts of material, radiochemical methods are employed, which have the considerable advantage over normal chemical methods that they enable the properties of the substance to be studied on an unweighable amount. The sensitivity of radiochemical methods is very high. By measuring the radiation it is possible to study the behavior of 10^3 to 10^4 atoms.

Of particular significance in the study of coprecipitation is the radiographic method, which enables the nature of the distribution of the substance in the solid phase to be made clear.

In carrying out coprecipitation reactions the state of those microquantities of substances which we wish to separate together with the solid phase is a very essential factor. Coprecipitation proceeds differently according to the degree of dispersion. If as a result of supersaturation or the formation of colloidal solutions the precipitate does not separate, this can be effected by precipitating it together with some other precipitate in the given solution.

Substances present in ultra-micro amounts behave similarily when the solubility product is not reached even for the most insoluble compounds, such as certain hydroxides and sulfides.

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1) L.I.Guseva and V.F.Leonov participated in this work.

If the substance is in solution in negligibly low concentrations, as would be the case, e.g., with radioisotopes, then in accordance with their nature the aqueous solutions will either be true or colloidal solutions. Radioisotopes are present in amounts which are not sufficient for the formation of particles of colloid size.

The capacity of radioisotopes to be trapped with a precipitate will differ according to whether they are in the form of radio colloids, molecules, or ions. The formation of radio colloids is determined by the low solubility of the respective components and their tendency to hydrolyze. The capacity of elements under given conditions to form an easily soluble complex compound will eliminate the formation of radio colloids. Since the concentrations of radio isotopes are very small, then in "trace chemistry", , adsorption plays an important role, particularly if the substance is in the form of a radio colloid.

Characteristics of the Properties and Composition of Sulfides

Heavy metal sulfides are the least soluble class of compounds used in analytical chemistry. By means of H_2S, the metals of the second and third analytical groups can be readily separated from many other metals, and traces of metals separated.

The concentration of acid in solution plays a very important part in the formation of sulfides. Such compounds as Bi_2S_3, PbS and CuS do not precipitate completely if the acid concentration is increased. As_2S_3, GeS_2, Re_2S_7, on the other hand, can only be precipitated at high values of the hydrogen ion concentration. This can be explained by the fact that As(IV), Ge(IV) and Re(VII) are in solution in the form of anions of the hydrogen acid or as undissociated weak acids. At high hydrogen ion concentrations it is natural to assume the presence of H_3S^+ cations which react with the anions of the acids indicated. Under these conditions HS^- and S_2^- ions do not play an essential part.

The structure (crystalline or amorphous) of the sulfides plays an important part in their precipitation, as well as the morphological form of the precipitate (powdery, flocculent, or gel-like), which depends on the conditions of formation and ageing. Considerable changes in the physical and chemical properties of the sulfides occur during ageing.

As examples we may adduce the α, β, γ forms of NiS which are obtained under different conditions and which differ from each other in structure and solubility. Cobalt sulfide also apparently exists in various crystalline forms which differ in their solubility.

There are two modifications for ZnS – α and β: the α separates from acid media while the β-form precipitates from alkaline media. The α-ZnS form differs from the β-form by a lower solubility in acid media, containing H_2S. Antimony sulfide (III) can also be obtained in different forms according to the method of precipitation. The forms which differ from each other most are the orange-red form, which is bulky and friable, and the black crystalline form, which has a higher density. The first of these forms of Sb_2S_3 is obtained under normal conditions, while the second is precipitated from strong HCl solutions. It is of interest to note that the black crystalline modification of Sb_2S_3 is purer than the orange one. The Sb_2S_3 which precipitates from HCl solution also contains the chloride which cannot be removed by washing.

Black mercuric sulfide is labile; it crystallizes in the normal system. On ageing, HgS is transformed into the stable modification with a red color and with a hexagonal crystalline form. The rate of transition from one form into the other depends on the acid concentration, temperature, and H_2S concentration.

One of the characteristics of the sulfides is the variability of the

composition of the precipitates formed, even when only one sulfide is concerned. Sulfides such as Hg_2S, CdS and PbS during their formation give compounds which differ in composition from the normal sulfides. On precipitating Hg in the presence of large amounts of HCl a compound of the composition $Hg_3S_2Cl_2$ ($2HgS \cdot HgCl_2$) is formed. This intermediate compound is also formed in sulfuric acid solutions of $HgCl_2$. However, on passing H_2S into a sulfuric acid solution of mercuric perchlorate, the above compound is not formed.

When cadmium is precipitated in the form of the sulfide from HCl solution, a precipitate is formed just as in sulfuric acid solution, which does not correspond to the formula CdS, but in addition contains cadmium chloride when precipitated from HCl solution and cadmium sulfate when precipitated from H_2SO_4 solution. The composition of the precipitates depends on the precipitation conditions. The effect of these characteristics of the sulfides has not been studied sufficiently; meanwhile, they are of great significance in the phenomenon of coprecipitation of these compounds.

Conditions for the Formation of Sulfides

The amount of various metals which is precipitated with the sulfides depends to a large extent on the conditions under which they are formed and on further changes during ageing.

Since the sulfides are only very slightly soluble, the rate of formation of their nuclei is large; the nuclei do not grow but give rise to a sol which coagulates after being formed. As a result of adsorption of S^{2-} and HS^- the sol has a negative charge. On coagulation of this kind of sol the cations are trapped by the precipitate. The number of cations trapped by the sulfide of a given metal depends on the dispersion of the sol and the charge of the cation.

The tendency of metals to coprecipitate is determined by the solubility of their sulfides and by other factors: isomorphism, the formation of chemical compounds, adsorption, etc..

Trapping by metal sulfides varies in accordance with precipitation conditions (H_2S concentration, rate and length of time for which the H_2S is bubbled through the solution). When H_2S water is used the amount of coprecipitation will depend on whether the initial salt is added to the solution or vice versa.

A rapid flow of H_2S for a long time yields precipitates with a large adsorbing surface. The effect of the H_2S concentration on the order of addition of the solutions during precipitation of sulfides by means of H_2S water on the precipitate is similar.

Apparently coprecipitation of metals with sulfides will be least when the crystalline structure of these compounds will be most clearly expressed. Separation of sulfides in a crystalline form can be achieved by slowing down the process of their formation.

Ostroumov and Maslennikova [1] prepared NiS and CoS in a crystalline form by precipitation in the presence of pyridine.

Sulfides can be precipitated by means of ammonium thiocarbamate [2].

Trapping of cations from solution by the sulfides continues after separation of the solid phase, and therefore the ageing of these precipitates affects the process considerably. Ageing, which is an important factor in the case of the sulfides, is related to a number of physico-chemical changes in these compounds, viz, changing over from an amorphous to a crypto-crystalline form, and change in the degree of aggregation and hydration. When sulfides which contain a large amount of water are dehydrated, their specific volumes change considerably.

From what has been said it follows that when studying the coprecipitation of metals with sulfides, each individual factor in the precipitation, though at first sight of little significance, should be carefully taken into consideration.

The Coprecipitation of Metals With Sulfides

The trapping of other ions from solution by precipitates was discovered long ago. It should be noted in this connection that a great deal of attention has been given to this phenomenon by Russian chemists, but nothing has been said in the literature till recently.

Even as long ago as 1886 the coprecipitation of considerable amounts of iron with sulfides of the platinum metals was observed by Vilm [3] while analyzing platinum ores.

A large number of investigations was subsequently devoted to a study of the precipitation of macro amounts of metals with sulfides. These experiments were the subject of disputes, both with regard to the possibility of preparing pure precipitates of these compounds during coprecipitation, and the reasons for coprecipitation.

In the opinion of N.A.Tananaev [4], during the precipitation of Cd and Hg or Zn and Cu by H_2S, formation is possible of compounds of the type of the sulfosalts - $CdHgS_2$ or $ZnCuS_2$, which are otherwise more soluble in acids than the sulfide compounds forming the given sulfo salt (analogous to Na_2HgS_2, which is soluble in water).

A number of investigations were carried out by Kolthoff and coworkers [5-9] on the trapping of metals of the third analytical group by sulfides of the second group. They consider that this phenomenon is the consequence of the subsequent precipitation which occurs as a result of the adsorption of H_2S on the sulfides of the H_2S group, which causes precipitation of the metals of the third groups.

In Fiegl's opinion [10] coprecipitation of metals of the third group with metals of the H_2S group occurs because of the subsidiary valency forces of sulfur. As the author points out, as a result of coprecipitation the following coordination compounds can be formed: a) hydrosulfides $MeS - SH_2$; b) polysulfides $MeS - S$, c) isopolymers $MeS - SMe$; d) heteropolymers $MeS - SMe_2$.

In connection with Fiegl's work it is of interest to note that in a paper published fairly recently by Fialkov and Muzyka [11] they reported the formation of polysulfides of the following composition: ZnS_4, ZnS_3, ZnS_2, CdS_3, CdS_4 and CdS_5, as a result of the interaction of salts of Cd and Zn with $(NH_4)_2S_2$ and $(NH_4)_2S_5$.

Ruffu and Hirsch [12] during their work on the fractional separation of metals also investigated the coprecipitation of metals of the third analytical group with the sulfides of the second. In their opinion, during the fractional separation of metals, the law of mass action and the solubility product are decisive factors. The formation of mixed crystals, occlusions, and adsorption are of little significance, according to them.

Balarev [13] reckons that the trapping of Zn by CuS is caused by internal adsorption of the zinc by the capillaries present in the particles of CuS.

The coprecipitation of micro amounts of various metals with the sulfides has found wide application for their separation and concentration. Chuiko [14] has carried out some systematic work along these lines. This author separated microgram quantities of copper with the following sulfides: CdS, PbS and SnS.

Gulyaeva and Itkina [15] separated small amounts of copper in the presence and in the absence of cadmium salts. The separation of copper on lead sulfide

has also been adopted by many authors [16].

Molybdenum sulfide, which is difficult to precipitate, has been separated with CuS [17].

In addition, investigations have been made on the separation of small amounts of copper on the sulfides of Cd, Pb, and Sn [18].

The coprecipitation of ultra micro amounts of metals with sulfides has been used for the study of the properties of substances at extreme dilutions, and also for the separation and purification of the radio isotopes of various metals.

Thus, during a study of the radio isotope Pb^{212}, it was separated by means of ammonium sulfide with Bi_2S_3 [19].

A similar investigation was carried out with Bi^{210} during its precipitation with PbS [20].

Bi_2S_3 [21] was used for a study of the relation between the capacity of Pb^{212} to precipitate and the solubility of lead salts.

This radio isotope of lead was also separated on Ag_2S prepared beforehand [22].

Pa^{231} was precipitated with Bi_2S_3 and PbS by means of $(NH_4)_2S$, and was separated from tin [23] in this way.

This radio isotope was separated with H_2S from acid media on the following sulfides: CuS, Sb_2S_3, HgS, and Bi_2S_3 [24].

In the course of a study of the coprecipitation of Th^{234} with FeS in the presence of $(NH_4)_2CO_3NH_4Cl$ [25] by means of $(NH_4)_2S$, it appeared that the FeS was inactive.

The properties of At^{211} were investigated by separating it with HgS from HCl media by means of H_2S [26].

Traces of Tc^{96} were coprecipitated from HCl media with PtS and Re_2S_7 [27], and also with CuS and MnS [28].

A considerable amount of work has been devoted to investigations of the coprecipitation of metals and sulfides. On the basis of these investigations, however, it can be concluded that in the strict sense of the word there is no theory of coprecipitation for a given class of compounds.

The question of the trapping of metals by sulfides has been solved by various authors in the course of investigations which have not been carried out under identical experimental conditions, as a result of which different explanations are put forward for the coprecipitation of one and the same metal with the sulfides. Moreover, these investigations have only been carried out with a limited number of metals, and only limited application of physico-chemical methods of analysis.

An explanation of the nature of coprecipitation, apart from its theoretical importance, is also extremely important for analytical chemical practice, since a knowledge of the sources of errors enables us to avoid them and to get practically pure analytical precipitates. Moreover, in this way it becomes possible to use H_2S for exact quantitative separation.

It is therefore desirable to start systematic investigations on the trapping of various metals by sulfides, in which the greatest possible number of combinations of precipitated metal-metal sulfide is considered, so that a general relation may be deduced.

It is essential that particular attention be given to a study of the conditions under which the sulfides are formed. A study of the coprecipitation

of sulfides is necessary, both for the separation of metals of the H_2S group from sulfides of the third group, and also for the study of the trapping of metals by sulfides, particularly in cases where we are dealing with very small amounts.

Special attention should be given to radio-chemical methods, which have exceptional possibilities in this field.

The present work is the first part of work done along these directions, in which results on the coprecipitation of Zn, Co, and Fe with the sulfides of the H_2S group are adduced.

EXPERIMENTAL

Salt Solutions Used

In order to carry out these investigations, 0.1 M solutions of the chlorides of Hg(II), Bi, Cd, Cu, Sb(III), Sn(II), Sn(IV), and of $AgNO_3$ and 0.02 M $PbCl_2$ were prepared. In experiments with arsenic a 0.1 M solution of sodium arsenite was used. Solutions of Zn, Co, and Fe(III) were also 0.1 M solutions of the chlorides of these metals. The solutions were standardized either gravimetrically or volumetrically. Copper was separated electrolytically. Chemically pure grades of the salts of the metals indicated above were used.

Precipitation of the Sulfides and Determination of the Amounts of Zn, Co, and Fe Trapped

During an investigation of the phenomenon of coprecipitation it is essential that all the conditions which can affect the amount of trapping of various impurities by the precipitate to some degree of another, should be carefully observed in order that reproducible results can be obtained. It is necessary, however, to observe that very often, even when all the conditions are reproduced exactly, the amount of material trapped can vary considerably in parallel tests. This becomes comprehensible if it is borne in mind that the process of formation of the solid phase, starting from the moment when the first nuclei appear to the appearance of the first opalescence, can take place at different rates. That this is so is indicated by the fact that it is necessary to add various amounts of precipitant in order to get the first appearance of turbidity. When coprecipitation is very marked, the amount of substance trapped in parallel tests shows variations which are well outside the limits of the accuracy of the gravimetric determinations.

The following factors were taken into consideration when choosing the precipitation conditions for the metals tested: rate at which H_2S is bubbled through the solution, temperature, acid concentration, and the time of standing of the solution plus solid phase before filtration. The experimental conditions just enumerated are essential factors in determining the structure, dispersion and composition of the precipitates, and thereby affect the extent of coprecipitation.

The application of radio isotopes for determining the amount of element coprecipitated has considerable advantages over the ordinary chemical methods. "Labelled" atoms enable the amount of coprecipitated metal to be determined directly from the activity of the precipitate. Thus the work is considerably simplified. The determination of metals on the precipitates of various sulfides is often a difficult problem, particularly if the given metal is present in small amounts.

It is essential, however, to note that in order to get correct results the radio isotopes used must be thoroughly purified themselves, so that it is possible to speak of radiochemical purity. In addition a number of blank tests must be carried out, in which various factors which can affect the accuracy of the

determination are taken into account, e.g., such factors as the screening action of the precipitate (particularly when using soft radiation); adsorption of the radio isotope by the filter; and the geometrical conditions used in measuring the activity.

Two series of experiments were carried out, in which ca. 10 mg and 100-200 mg lots of sulfides were precipitated, respectively. In the first case the amounts of Zn, Co and Fe were small, while in the second case they were present in equimolar amounts.

The experiments with the small amounts were carried out as follows: To a 25 ml flask were added 0.1 m-mole of the solution of the metal of the fourth or fifth group, 0.5 ml of a solution of the radio isotope, and HCl added until its final strength was 0.3 N[1], and the contents of the flask made up to 25 ml with distilled water. H_2S was passed through the solution after being preliminarily passed through a wash bottle containing water. The H_2S rate was 50-60 bubbles per minute, the temperature of the solution being 18-20°. Filtration was carried out under pressure 18 hours after precipitation, through a close grained filter 3.5 cm in diameter and with a 6-7 mm edge. The filter was placed in a funnel with a porous plate. The precipitate was washed 8-10 times with 3 ml of a 0.1% ammonium chloride solution saturated with H_2S.

After drying the filters were placed in tracing cloth envelopes, and their activities determined. The activity of 0.5 ml of a solution of the respective radio isotope placed on a filter and prepared in the same way was measured in parallel. The amount of radio isotope adsorbed by the filter under our experimental conditions and the screening activity of the sulfide precipitates were determined in separate experiments. The percentage coprecipitation was then determined from these results.

The labelled atoms used were the following radio isotopes: Zn^{65}, Co^{60}, and Fe^{59}. They were carefully purified before use. The solutions of $Zn \cdot Cl_2$, $Co \cdot Cl_2$ and $Fe \cdot Cl_3$ were used in amounts corresponding to the following ratios in the precipitation solution: Zn^{2+} : Me^{2+}, Me^{3+} = 1:12; Co^{2+} : Me^{2+}, Me^{3+} = 1: 5,000; and Fe^{3+} : Me^{2+}, Me^{3+} = 1.6:10.

The radioisotopes were purified as follows: Zn and Co were reprecipitated several times, while the ferric chloride was purified by repeated extraction with ethyl ether. In the case of zinc the reaction selected for purification was precipitation in the presence of iron salts with alkali, and subsequent separation as the sulfide at a pH of 2-3. Cobalt was purified by precipitation in the form of potassium cobaltinitrite and α-nitroso-β-naphthol.

The 0.5 ml of a solution of the radio isotope indicated gave ca. 15,000 impulses/minute. Preparations with low activity were measured for 20-30 minutes.

The relative error of measurement was calculated from the formula

$$\delta' = \frac{\delta E}{E} = \frac{0.67}{E} \sqrt{\frac{E + \Phi}{t_1} + \frac{\Phi}{t_2}}$$

where δ' is the relative error of the result, δE the error of measurement, E the number of impulses per unit time, t_1 the time during which the activity of a preparation was measured, t_2 background, and Φ the number of impulses of the background.

Calculation shows that in this way it is possible to determine 0.1% of the metals indicated above (see Table 1).

---

1) In experiments with Ag_2S precipitation was effected from 0.3 N HNO_3.

In experiments with large amounts of sulfides the precipitation was carried out from 100 ml, the H_2S being bubbled through for 15 minutes. 10 ml of 0.1 M solutions of the respective metals of the H_2S group and 10 ml of 0.1 M $ZnCl_2$, $CoCl_2$, and $FeCl_3$, respectively, were used for precipitation. The amount of Zn, Co and Fe trapped was determined from the amount left unprecipitated, either gravimetrically or volumetrically.

In the remaining cases the experiments were carried out in a similar way with small amounts of sulfides.

TABLE 1

Coprecipitation of small amounts of zinc, cobalt, and iron with the sulfides of the metals of the H_2S group

No.	Metal sulfide	Found in the ppt. in %		
		Zn	Co	Fe
1	HgS.....	0.8	3.2	0.14
2	CuS.....	0.7	0.11	0.10
3	CdS.....	7	0.10	0.19
4	Bi_2S_3.....	0.4	0.10	0.15
5	SnS_2.....	10	17.20	1.81
6	SnS.....	–	2.20	0.50
7	Sb_2S_3.....	0.3	0.12	0.15
8	As_2S_3.....	0.4	<0.10	0.16
9	PbS.....	0.3	<0.10	0.15
10	Ag_2S.....	0.2	<0.10	0.10

TABLE 2

Coprecipitation of equimolar amounts of zinc, cobalt, and iron with the sulfides of the metals of the H_2S group

No.	Metal sulfide	Found in the ppt. in %		
		Zn	Co	Fe
1	HgS.....	40.2	5.5	<0.3
2	CuS.....	11.2	0.5	2.4
3	CdS.....	9.5	3.4	3.2
4	Bi_2S_3....	3.7	2.5	0.5
5	SnS_2.....	3.0	8.1	8.9
6	SnS.....	1.9	1.5	2.0
7	Sb_2S_3....	1.5	2.1	6.5
8	As_2S_3....	1.1	1.0	2.8
9	PbS.....	0.5	1.1	1.6
10	Ag_2S.....	<0.3	<0.3	<0.3

The results, which are adduced in Table 1, show that the amount of Co and Fe trapped by almost all the sulfides of the fourth and fifth groups is very small. The exception is SnS_2, with which a considerable amount of Co is precipitated.

The amount of Co precipitated with HgS and of Fe with SnS_2 is fairly high. Considerably more Zn is trapped in the precipitate as compared with Co and Fe. According to these results the coprecipitation of Zn with CdS and SnS_2 is especially marked.

It is interesting to mention some of the observations made during these experiments, the results of which are given in Tables 1 and 2.

After precipitation of the sulfides, a clear cut difference was observed in the volume occupied by a given precipitate. The outstanding precipitate was Sb_2S_3, which had the greatest volume. The sulfides of Hg (II), Pb, Ag, and Cd, on the other hand, had the least volume of all the sulfides; the volume of these sulfides was several times less than that of Sb_2S_3. The volumes of the precipitates of the other sulfides were intermediate between the volumes of the four sulfides mentioned above and that of Sb_2S_3.

Filtration of the sulfides was satisfactory, with the exception of SnS_2. The SnS_2 precipitated in the presence of Co had a brownish yellow color, and not the usual yellow color. In this case coprecipitation is much more marked as compared with the other sulfides.

Discussion of Results

The general conclusion which follows from a comparison of Tables 1 and 2 is that the amounts of Zn, Co, and Fe trapped by the precipitate for small amounts of Zn, Co, and Fe are considerably less than when large amounts of these three elements are present. The behavior of Co during the precipitation of SnS_2 (see

Experiment 5, Table 1 and 2) is of interest in this connection; for small amounts of Co the amount of coprecipitation is considerably greater than when large amounts of Co are present.

The results in Table 2 show that when Zn, Co, and Fe are present during the precipitation of the H_2S group of elements, coprecipitation varies for any given metal of this group. Thus, those conditions which are usually recommended in analytical textbooks, i.e., precipitation from a solution 0.3 N with respect to acid, do not lead to a complete separation of these metals. Coprecipitation is particularly marked in the case of Zn and HgS, where it amounts to 40%.

It is of interest to note that Co and Fe coprecipitate with SnS_2 in large amounts, while the extent of coprecipitation with SnS is low. This is probably the result of oxidation of Sn from the bivalent to the quadrivalent stage. On comparing the crystalline lattices of SnS_2 and SnS it appears that SnS has a rhombic lattice, while SnS_2 has a hexagonal one. The sulfides of Co and Fe also have a hexagonal lattice. This apparently also explains the large difference between the coprecipitation of the two metals with SnS_2 and SnS.

A similar phenomenon can be observed in the coprecipitation of Zn with HgS. Both the HgS and ZnS have a cubic lattice. It should be borne in mind that HgS immediately after precipitation has a hexagonal lattice, but this subsequently changes into a modification having a cubic lattice.

The fact that, as a rule, in our experiments coprecipitation occurs to a lesser extent for small amounts of Zn, Co, and Fe is of interest. In this connection, therefore, the question arises as to why, in the experiments with Sn(IV) for small amounts of Co, does coprecipitation increase considerably. An explanation of this fact may be sought in an increase in the relative adsorption with decreasing concentration of the trapped ion.

Investigation of the coprecipitation of sulfides continues. It is necessary to point out that in order to make a deeper study of this phenomenon it is essential that such methods as radiography, electron microscopy, and X-ray spectrography be used, whereby the relations between coprecipitation and structure, dispersion, and the conditions of formation of a given sulfide can be established.

In addition, special attention must be given to a study of the actual process of formation of the sulfides, using photographic methods for this purpose.

In conclusion I should like to express my thanks to Prof. I.P.Alimarin for directing the work.

SUMMARY

1. During the precipitation of 10^{-3} mols of HgS, PbS, SnS_2, SnS, CdS, CuS, and $0.5 \cdot 10^{-3}$ mols of Bi_2S_3, As_2S_3, Sb_2S_3 from 0.3 N HCl and of Ag_2S from 0.3 N HNO_3 in the presence of equimolar amounts of $ZnCl_2$, $CoCl_2$, and $FeCl_3$, coprecipitation of these metals occurs.

2. Coprecipitation was most marked for the following metals: Zn with HgS (40.2%); CuS (11.2%); CdS 9.5%; Bi_2S_3 3.7%; SnS_2 3%; Co with SnS_2 8.1%; HgS 5.5%; CdS 3.4% and Fe with SnS_2 8.9%; Sb_2S_3 6.5%; CdS 3.2%; As_2S_3 2.8%.

3. Coprecipitation is least for Zn, Co, and Fe with Ag_2S (<0.3%). Coprecipitation varied in the remaining cases from 0.5-2%.

4. During precipitation of the sulfides indicated above in amounts of $0.5 \cdot 10^{-4}$-10^{-4} mols in the presence of small amounts of Co and Fe, the amount of coprecipitation observed for these metals was insignificant (0.1-0.2%), with the exception of SnS_2 and HgS. The coprecipitation of Co with SnS_2 amounts to 17.2%, of Fe 1.81%, and for Co with HgS to 3.2%.

Zn is trapped to a far greater extent than Co and Fe, particularly with CdS 7% and with SnS_2 10%.

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THE ULTRA-MICRO METHOD OF CHEMICAL ANALYSIS

COMMUNICATION 2

THE ELECTROLYTIC SEPARATION AND DETECTION OF METALS

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By using the apparatus for ultra-microchemical determinations and the corresponding auxiliary apparatus [1,2], it is possible to examine small volumes of solutions (10^{-3} - 10^{-4} ml) by means of various analytical methods.

The apparatus and experimental technique for analysis by ultra-micro methods have a specific character. The procedures adopted for the simplest chemical operations (filling flasks with liquids, pouring from one to the other, measuring the requisite volumes, precipitations, etc..) and the apparatus necessary for these procedures, have been adequately described [2]. However, in order to carry out a qualitative analysis of some object or other, more diverse forms of apparatus are necessary, as well as a greater number of operations.

The electrolytic deposition of metals from solution is an excellent method for separating and detecting the elements. By means of special apparatus and the respective techniques, electrolysis can be carried out using the microscope both with solid [3,4] and with liquid electrodes. It should be noted, however, that the application of electrochemical methods to the ultra-micro analysis of inorganic compounds has not yet been described.

The question of what is the minimum amount of a metal which it is necessary to have in solution in order to deposit it electrolytically can be solved by means of Nernst's equation. A calculation for the case of copper ions gives the following results, the deposition potential of copper from a normal solution is 0.34 V. In view of the fact that the hydrogen overvoltage on copper is 0.23 V, then the potential of the cathode can be adjusted to this value. At such a potential the copper ion concentration in solution will be given by:

$$-0.23 = 0.34 - \frac{0.058}{2} \log \frac{1}{c}; \quad 0.57 = 0.029 \log \frac{1}{c},$$

from which $c = 10^{-20}$. This concentration is outside the limits of any qualitative determination.

In order to deposit any element electrolytically certain conditions must be observed. The potential during electrolysis even in the ultra-micro method must naturally in any case be not less than the decomposition potential of the electrolyte. As a result of the small surface of the electrodes used in ultra-micro methods, the necessity of observing a definite value for the current density (0.1 - 0.01 A/cm^2) means using a current density of 10^{-4} + 10^{-5} A.

Electrolysis With Platinum Microelectrodes

Platinum electrodes possess the advantage that they exclude the possibility

of contamination of the solution with foreign ions during electrolysis. In ultra-micro methods, therefore, they are given preference to solid electrodes made from any other metals.

a) Apparatus

The electrolytic deposition of metals from small volumes of the order of 1 λ (10^{-3} ml) can be effected by using special micro apparatus which differs from the apparatus used for macro electrolysis in that part of the apparatus where electrolysis actually occurs. The electrical set up is left practically unchanged; the current flows from an accumulator (a 4-6 volt source of D.C.), through a switch resistance box into an electrolytic micro cell.

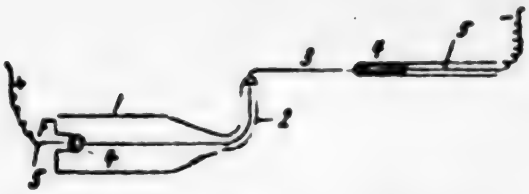

Fig. 1. Electrolysis on a condenser rod. 1 – condenser rod; 2,3 – electrodes; 4 – mercury contacts; 5 – current leads.

Electrolysis using platinum micro electrodes can be carried out by two methods:

1. The test solution is placed on the end surface of a thick walled capillary (external diameter ca. 5 mm, internal diameter 0.5 mm) in the form of a condenser rod [2] (Fig. 1), into the bore of which has been fused a platinum wire of diameter ca. 0.1 mm, one end of which finishes up in the end surface of the condenser rod and serves as the anode. The other end of this wire is located inside the capillary at some distance from its other end; mercury is introduced into the bore of the capillary from this side so that the anode is in contact with the lead-in for the current. The cathode is also a platinum wire fused into an ordinary capillary (Fig. 1) so that one end sticks out of the capillary, while the other is located inside the capillary. A small drop of mercury is placed on the capillary so that contact is established between the cathode and the lead-in for the current. The end which sticks out is bent at right angles over a small length of the wire and serves as the cathode. The capillary is mounted in a glass tube. When an electrolytic cell of this kind is used, a humidity cabinet of a different design to that described previously is required [1,2]. The brass walls of the cabinet are not unbroken rods all along their length; instead they have rods of 1 cm at each of the four corners of the cabinet, in which grooves are made as well as in the unbroken walls (Figs. 2, 3).

2. The test solution is placed in an ordinary micro-cone [1,2], and two platinum rods fixed in it. The electrodes in this case are platinum wires ca. 0.1 mm in diameter, fused into a glass tube and insulated from each other (Fig. 4). The current is led in through a copper wire which is pressed on to the platinum wires. Electrodes of this type are made as follows; two platinum wires (1) of the requisite length (2-2.5 cm) are connected to two copper wires (2) by pressing; the contact is made more reliable if a crystal of silver nitrate is placed at the junction between the copper and platinum and heated in a micro flame to reduce the silver. The wires thus obtained (3) are fixed in a glass capillary, only ca. 1 cm of the end of the platinum wires being left free. The whole is then mounted in a glass tube (4). A plastic cap (5), chosen so that it corresponds in diameter to the tube, is then fixed at the end of the tube where the copper wires are located, and the copper wires fixed through the cap. The platinum wires are bent as shown in Fig. 4. In this form the electrodes are ready for use.

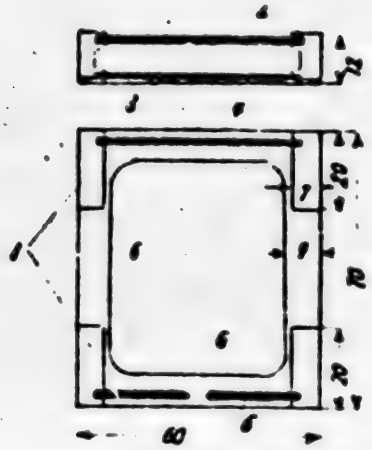

Fig. 2. Cabinet for carrying out electrolysis on the condenser rod.

1, 6 - brass walls and frame; 2, 3, 4, 5 - glass covers, bottom and walls.

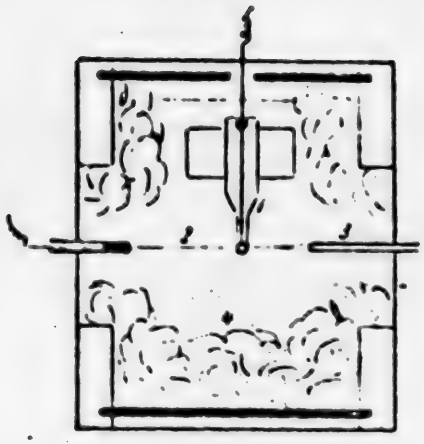

Fig. 3. Arrangement of the apparatus for carrying out electrolysis on the condenser rod.

1 - condenser rod; 2 - platinum electrodes; 3 - micro pipet; 4 - damp cotton wool.

Procedure For Electrolysis

1. Electrolysis on the condenser rod. The condenser rod and the anode fused to it are fixed to a cover glass and placed in a humidity cabinet (Fig. 3). The cabinet is fixed on the objective stage of the microscope so that its brass walls are turned toward the manipulators, while the part of the condenser rod which ends up in the surface where the electrolysis is conducted is turned toward the observer (Fig. 3). The current leads are fixed in the mercury contacts of the anode and cathode. An ordinary humidity cabinet containing the necessary micro flasks is placed on top of the cabinet containing the condenser rod set up for electrolysi

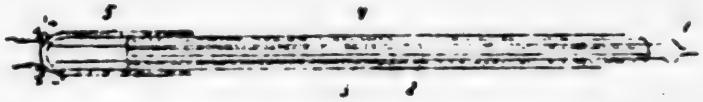

Fig. 4. Forked platinum electrodes.

1 - electrodes; 2 - copper wires; 3 - insulated capillaries; 4 - glass tube; 5 - plastic cap.

The cross-over arrangement of the cabinet thus obtained is suitable for leading the cathode up to the condenser rod, and for illuminating the latter. The illumination in this case is arranged so as to be level with the condenser rod in its cabinet, and the light falls on the surface F of the rod (Fig. 1). The piston and pipet set-up is fixed in the right hand claw of the manipulator [1]. When the apparatus has been arranged in this way we can proceed with the electrolysis. The flask (i.e. capillary tubes, etc.) which are in the upper cabinet are filled with the necessary solutions. A definite amount of the requisite solution is then sucked up in the micro pipet and removed from the cabinet, it is then lowered by means of the micro manipulator to the level of the gap in the lower cabinet.

The upper cabinet is removed and the surface of the condenser rod on which the electrolysis occurs is introduced into the field of vision, and the microscope focussed. The solution in the pipet is transferred on to the electrolysis surface. By means of the naked eye and by observation through the microscope the cathode is brought up to the illuminated surface and arranged above it without actually touching the solution. The accumulator is then connected to the electrolysis cell. The left hand manipulator is lowered and the cathode immersed in the drop on the illuminated electrolysis surface, thus completing the circuit. Electrolysis is initiated and its course followed under the microscope, (bubbles of gas are visible). That electrolysis has finished is checked by a negative reaction with the respective reagents. This reaction is carried out on the illuminated surface of the usual condenser rod [2] in another cabinet by placing on the surface of the rod a small amount of solution taken from the surface where electrolysis was carried out, and adding the respective reagent to this portion. When electrolysis is complete the circuit is opened by lifting up the cathode with the manipulator, thereby removing it from the solution. The current is then switched off. The metal which has been deposited is determined by its characteristic color, or by means of special reagents after it has been dissolved in acid.

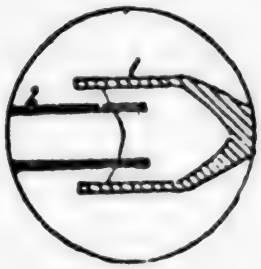

Fig. 5. Electrolysis with forked platinum electrodes (as seen under the microscope).

1 - micro-cone + electrolyte; 2 - electrodes.

2. Electrolysis on a micro-cone. The micro apparatus containing the requisite solutions and the micro-cone which serves as the electrolyzer are placed in the humidity cabinet. The diameter of the micro-cone should be such that, when the electrodes are inserted into it, they do not touch the walls of the micro-cone. If the electrodes are almost touching the walls, then the solution which is displaced on immersing them will flow along the walls, so that all of the solution is not electrolyzed. It is essential also that the length of the electrolyzer should not be more than 4-5 mm; in such a case only a small part of the electrodes will be located in that part of the electrolyzer not filled with solution, and which amounts to a third of its volume. The cabinet and the micro cell are fixed on the object stage of the microscope. The platinum electrodes (Fig. 4) are fixed in the left hand claw of the manipulator, while the piston set-up and pipet are fixed in the right hand claw. A volume of solution is transferred from the micro flask to the electrolyzer by means of the pipet, the volume being such that it does not occupy more than two thirds of the volume of the micro cell, in order that spilling may be avoided during electrolysis. The opened side of the humidity cabinet is turned toward the left hand manipulator and then, first by means of the naked eye and finally with the aid of the microscope, the electrodes are introduced into the electrolyzer without actually immersing them in the solution. The current is switched on and the electrodes then immersed in the solution by moving the electrolyzer on to them (Fig. 5), thereby completing the circuit. When electrolysis is finished the circuit is broken by removing the electrodes first from the electrolyzer and then from the cabinet, by means of the manipulator. Finally the current is switched off. The metals which have been electrolytically deposited in this way are detected as described above.

b) Examples of electrolytic deposition and detection of metals

1. Deposition of copper on a platinum cathode. A solution of cupric sulfate

(1 mg/ml) was prepared in 0.2 M H_2SO_4. The current necessary is calculated from a knowledge of the surface area of the electrodes and the recommended current density. Electrolysis is carried out as described above on the illuminated surface of a condenser rod or in a micro-cone electrolyzer. The deposit of copper formed on the cathode is examined under the microscope in reflected light. If the layer of copper which separates out on the given surface is so thin that its color cannot be observed, then the electrode is immersed for some time in a flask containing nitric acid. The copper is then detected in the solution by means of either sodium diethyldithiocarbamate or rubeanic acid.

Copper can be deposited electrolytically in the same way from solutions containing other metals (e.g., iron, zinc, nickel). Results for the electrolytic separation of copper from solution are adduced in Table 1.

2. Deposition of lead dioxide on a platinum anode. A solution of lead nitrate is used (1 mg/ml of Pb). Electrolysis was carried out as described above at 2.7 V using a current of 10^{-4} A. The brown film of lead dioxide which is formed on the anode can be clearly distinguished under the microscope in reflected light. The solutions left after electrolysis gave negative reactions with dithizone. Results on the deposition of lead dioxide on a platinum anode are given in Table 1.

TABLE 1

Separation of copper and lead on platinum micro electrodes

No.	Electrolyte: Composition	Electrolyte: Metal concentration, (g/ml)	Electrolyte: Volume, (ml)	Electrodes: Diameter (cm)	Electrodes: Surface area, in cm^2	Conditions of electrolysis: Voltage, in V	Conditions of electrolysis: Current, in amp.	Conditions of electrolysis: Time, in min.	Electrolysis products: Composition	Electrolysis products: Amount, in g
1	$CuSO_4$	$1\cdot10^{-3}$	$1\cdot10^{-3}$	0.01	$\sim10^{-3}$	2.2	10^{-4}	10	Cu	$1\cdot10^{-8}$
2	$CuSO_4$	$1\cdot10^{-3}$	$0.5\cdot10^{-3}$							
	$NiSO_4$	$1\cdot10^{-3}$	$0.5\cdot10^{-3}$	0.01	$\sim10^{-3}$	2.2	10^{-4}	10	Cu	$5\cdot10^{-7}$
	$FeSO_4$	$3\cdot10^{-4}$	$0.5\cdot10^{-3}$							
3	$CuSO_4$	$1\cdot10^{-3}$								
	$NiSO_4$	$1\cdot10^{-3}$	$0.5\cdot10^{-3}$	0.01	$\sim10^{-3}$	2.2	10^{-4}	10	Cu	$1\cdot10^{-7}$
	$FeSO_4$	$3\cdot10^{-4}$								
	$ZnSO_4$	$1\cdot10^{-3}$								
4	$CuSO_4$	$5\cdot10^{-5}$	$1\cdot10^{-3}$	0.01	$\sim10^{-3}$	2.2	10^{-4}	10	Cu	$5\cdot10^{-8}$ 1)
5	$Pb(NO_3)_2$	$1\cdot10^{-3}$	$0.5\cdot10^{-3}$	0.01	10^{-3}	2.7	10^{-4}	10-15	PbO_2	$5\cdot10^{-7}$

1) The copper which separated out on the cathode in this case was detected after dissolving it in acid, by means of sodium diethyldithiocarbamate or rubeanic acid, since direct observation of the copper color on the cathode was impossible because the copper layer was too thin.

Electrolysis on a mercury micro cathode

Electrolysis in which a mercury cathode is employed is very widely used in analytical chemistry because it enables such metals as chromium, iron, and molybdenum, which are not deposited on platinum electrodes, to be separated. Mercury occupies a unique position as cathodic material, since it requires different apparatus and different technique. In addition, the process of electrolysis on a mercury cathode is accompanied by intense evolution of gas bubbles, and heating

of the solution. These two factors give rise to a number of difficulties when working on the ultra-micro scale.

a) Apparatus

Electrolysis on a mercury cathode is carried out in a capillary open at both ends because of the intense gas formation which occurs during electrolysis and which would lead to the solution being expelled if the electrolysis were conducted in the usual type of cell.

The mercury cathode is prepared by covering a platinum fork (Fig. 4) electrolytically with mercury (in order to do this it is only necessary to join the copper leads at the place where the current is supplied to electrodes). A platinum wire fused into the same glass tube serves as the anode. In order to prepare the mercury micro cathode, a solution of mercuric nitrate (0.1 g in 0.05 ml of HNO_3 and 5 ml H_2O) is used. Electrolysis is carried out in a micro-cone until a drop of mercury is formed on the fork. Electrodes prepared in this way can be used for electrolysis on a mercury cathode (Fig. 6). The current for anode and cathode is first led from the accumulator to a switch resistance box.

b) Procedure for electrolysis on a mercury micro cathode

The micro apparatus required to hold the necessary solutions and the capillary open at both ends are placed in a humidity cabinet on a stand [1, 2]. The capillary electrolyzer should be of such a diameter that when the electrodes are introduced into it, they do not touch the walls. The cabinet is fixed on the objective stage of the microscope. The tube containing the electrodes is clamped in the left hand manipulator in such a way that the anode is above the cathode, while the piston set-up and pipet are clamped in the right hand manipulator. The micro vessels are filled with the requisite solutions and measured amounts of them transferred to the capillary, in which the solution is arranged so that it is at a distance of about a third of the length which its volume occupies from the end of the capillary turned toward the pipet. The cabinet with the opened side is then turned towards the left hand manipulator. Initially the electrodes are adjusted by means of the naked eye and finally with a microscope in the capillary electrolyte, without actually immersing them in the solution. The current is switched on and the circuit completed by moving the capillary on to the electrode until the latter just touches the farther meniscus of the solution. The course of the electrolysis is followed under the microscope. The completion of electrolysis is tested for by means of the requisite reagents. When it has finished, the electrodes are withdrawn from solution, and the current switched off.

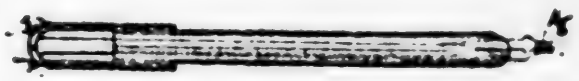

Fig. 6. Mercury micro cathode.

After deposition of the metal on the mercury cathode the mercury is removed by including the cathode in a circuit used as a micro heater [2]. The metals which remain on the fork after removal of the mercury can be dissolved by immersion in

a micro-cone containing the respective solvents, and the metals subsequently detected in solution.

c) Examples of the separation of metals on a mercury micro-cathode

1. Separation of vanadium from copper and iron. Solutions of cupric sulfate, ferrous sulfate, and ammonium vanadate in 2N sulfuric acid were prepared.

The voltage normally used for macro-electrolysis on a mercury cathode cannot be recommended for the electrolysis of small volumes, since when such a voltage is used electrolysis proceeds so turbulently that within a very short time all the solution would be splashed out and evaporated. Vanadium is separated from copper and iron at a voltage of 3.3-3.8 V, with a current of $3.3\text{-}3.8\cdot10^{-4}$ A. Electrolysis is stopped when the electrolyte gives a negative reaction with potassium ferro- and ferricyanide. The presence of vanadium is detected by means of cupferron solution. The volumes of solutions and the amounts of material used for electrolysis are adduced in Table 2.

2. Separation of vanadium from chromium. Solutions of potassium chromate and ammonium vanadate in 2N sulfuric acid were prepared. Electrolysis was carried out as described previously at a voltage of 3.4-3.6 V and a current of $3.4\text{-}3.6\cdot10^{-4}$ A. Electrolysis was stopped when the solution gave a negative reaction for chromium with diphenyl carbazide. The volumes and weights of materials used are adduced in Table 2.

TABLE 2

Separation of elements by electrolysis on a mercury micro-cathode

No.	Electrolyte			Cathode surface, in cm^2	Electrolysis conditions			Deposit on cathode		Left in solution (Sol.)	
	Composition	Metal concentration (g/ml)	Volume, in ml		Voltage, in V	Current, in A	Time, in min.	Metal	Amount, in g	Element	Amount, in g
1	$CuSO_4$	$1\cdot10^{-3}$	$0.5\cdot10^{-3}$	$2\cdot10^{-3}$	3.8	$3.8\cdot10^{-4}$	15	Cu	$5\cdot10^{-7}$	–	–
	$FeSO_4$	$3\cdot10^{-4}$	$0.5\cdot10^{-3}$					Fe	$1.5\cdot10^{-7}$	–	–
2	$CuSO_4$	$1\cdot10^{-3}$	$0.3\cdot10^{-3}$	$2\cdot10^{-3}$	3.8	$3.8\cdot10^{-4}$	15-20	Cu	$3\cdot10^{-7}$	–	–
	$FeSO_4$	$3\cdot10^{-4}$	$0.5\cdot10^{-3}$					Fe	$1.5\cdot10^{-7}$	–	–
	NH_4VO_3 (H_2SO_4)	$2\cdot10^{-4}$	$0.7\cdot10^{-3}$					–	–	V	10^{-7}
3	NH_4VO_3 (H_2SO_4)	$2\cdot10^{-4}$	$0.5\cdot10^{-3}$	$2\cdot10^{-3}$	3.6	$3.6\cdot10^{-4}$	15	–	–	V	10^{-7}
	$K_2Cr_2O_7$	$2\cdot10^{-4}$	$0.5\cdot10^{-3}$					Cr	$1\cdot10^{-7}$	–	–

SUMMARY

1. Apparatus and methods have been developed for the electrolytic separation and detection of elements on the ultra-micro scale.

2. Procedures are described for ultra-micro electrolysis using platinum and mercury electrodes in solution with volumes of the order of 10^{-3} ml and with amounts of material of the order of 10^{-6} to 10^{-8} g.

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CRYSTALLINE LIGHT FILTERS FOR THE ULTRA-VIOLET REGION OF THE SPECTRUM [1]

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In the course of scientific research, and in seeking for the solutions of a number of practical questions, it often becomes necessary to separate fairly narrow bands in the ultraviolet region of the spectrum in the spectrum of the light source. This is usually achieved either by using monochromators, which are rather expensive and complicated, or by means of various types of light filters. The difficulties which confront investigators working in this spectral region when selecting the requisite light filters are well known, despite the fact that a large amount of work [1, 2] has been devoted to light filters suitable for the ultraviolet.

In most cases liquid light filters, which are solutions of various chemicals, are used for the isolation of individual bands in the ultraviolet. Liquid light filters, however, have rather wide transmission bands, and they considerably weaken the light isolated. Slight contamination of the solutions leads to an even greater decrease in the transmission coefficient. Many of these solutions, once exposed to the ultra-violet, deteriorate on storage, and the filters cease to transmit the necessary spectral band.

Peskov's light filter [3], in which a gaseous mixture of bromine and chlorine is used as the absorbing material, is of special interest. This filter is fairly constant, and is used for the isolation of a wide band of wave lengths in the ultra-violet from 2600-3000 A. More frequently, however, it becomes necessary to isolate a narrow band or individual lines from a line spectrum with a fairly high transmission coefficient. Gas filters are obviously unsuitable for such purposes.

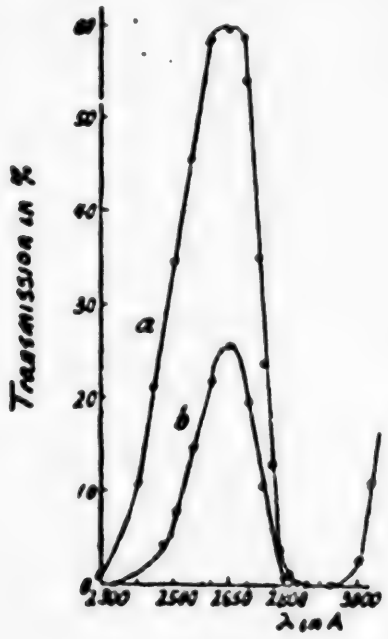
In the course of the present investigation we studied the absorption spectrum of mixed crystals of the alkali halides with the objective of constructing narrow band crystalline filters for the ultra-violet.

The alkali halides find wide application in optics on account of their transparency to the ultra-violet, visible and infra red spectral regions. Good transparency, however, is a characteristic of only very pure crystals. The presence in the crystals of even insignificant amounts of impurities, sometimes not more than a thousandth of a percent, lead to supplementary absorption in the crystals. Investigation [4, 5] of the absorption spectra of crystals of the alkali halides containing various impurities has shown that in addition to the characteristic absorption bands of the crystals themselves in the ultra-violet, absorption bands which are caused by the impurities can be observed. These absorption bands are ascribed [6] to the ions of the impurity, and appear in the spectrum as the result of an electron transfer from a fundamental level of the ion to an excited level. The position of the band caused by the impurity, in the absorption spectrum of the crystal, and the form of this band, is determined by the nature of this impurity, while the absorption coefficient is determined by the amount of impurity. With increasing concentration, the impurity absorption maximum increases. One and the same impurity, when present in various alkali halide crystals, gives rise to absorption bands which are located in different parts of the ultra-violet. Thus, Tl as an impurity in KCl, KBr, and KI crystals, respectively, gives rise to maximum absorption at 2475, 2610 and 2870 A, respectively. Pb in KBr crystals gives rise

1) Presented at the Leningrad Physico-Technical Institute, Academy of Sciences, USSR, in 1951.

to a maximum absorption in the KBr absorption spectrum at 3020 A. Pb and Tl as impurities in other crystals of the alkali halide salts also lead to the appearance of absorption bands which are characteristic of the impurity, but are located in other parts of the spectrum. In mixed crystals the position of the absorption band depends on the concentration of the components. Thus, if an impurity of a different kind is introduced into the crystals of the alkali-halide salts, it is possible to get absorption bands for the impurity at various points in the absorption spectra, according to which alkali halide salt the impurity has been added, and according to the nature of the impurity. These great possibilities of getting absorption bands at various points in the ultra-violet absorption spectrum, and also the exceptional definition of the absorption band, enable one, by using combinations of crystals with various impurities, to separate narrow transmission bands in the ultra-violet. It seemed to us, therefore, that crystals of alkali halide salts containing impurities could be used for constructing narrow band light filters for the ultra-violet.

When impurities are added to mixed crystals, the absorption bands which arise as a result of the presence of impurities are displaced in the spectrum (as already indicated) in accordance with the various percentages of the components of the mixed crystals; consequently, the position of the transmission band of the crystalline light filters will also be determined by the concentrations of the components of the mixed crystals. This last fact enables one, within known limits, to shift arbitrarily the transmission bands of the light filters along the spectrum, and thus makes it possible to construct crystalline light filters for the requisite wave length.



As an illustration of the possibility of constructing light filters for the ultra-violet, we adduce the absorption spectra of the mixed crystals KCl + KBr (Curve a in the diagram) containing an equal amount of the components, and Pt as an impurity. It is evident from the diagram that the mixed crystals KCl + KBr have a clear cut transmission band within the ultra-violet, with maximum transmission at 2625 A. The transmission coefficient for this wave length is more than 80%. In addition to its transparency to the ultra-violet, this crystal is transparent to light of wave length greater than 3000 A. Therefore, when the mixed crystal KCl + KBr is used as a light filter, it is necessary to use a supplementary filter, with good transmission in the 2600 A region, and which absorbs the long wave length part of the absorption spectra of the crystal (starting at 3000 A). In such a case the gas filter (considered above) which absorbs in the 3000-5000 A region can be used as a supplementary filter. The transmission of the crystal KCl + KBr and of the gas filter working together, as can be seen from the transmission curve (Curve b in the diagram), consists of only one narrow band in the ultra-violet.

Thus, an optical system consisting of the mixed crystal KCl + KBr with Pb as an impurity and the gas filter as a supplementary can be used as a light filter with a high luminosity and with a narrow transmission band. The transmission coefficient of this light filter at 2650 A amounts to 26% for a half width of the

transmission band of about 170 A.

A narrower transmission band at 2600 A is given by a combination composed of a crystal of KCl containing Tl and Pb, the mixed crystal KCl + KBr containing Pb, and the gas filter. The transmission coefficient in this case at 2625 A amounts to 14% for a half width of the transmission band of only 85 A.

KI containing Tl in combination with a gas filter exhibits a maximum transmission band at 2750 A. The transmission coefficient of this light filter is 26% for a half width of the transmission band of about 200 A.

The transmission bands can be narrowed by using as a supplementary filter the mixed crystal KCl + KBr containin Tl. This crystal cuts out the short wave part of the transmission band, and, by varying the proportion of KBr, transmission bands of different widths can be obtained.

For isolating a band at 2850 A, a filter can be used which is composed of a crystal of KBr + KI (containing Tl + Pb), plus a gas filter. The transmission of the gas filter which we had at our disposal was low (ca. 25%) at 2850 A; consequently the light filter consisting of a crystal of KBr + KI and a gas filter has a transmission coefficient of only 10% at 2850 A for a half width of the transmission band of 120 A. Increasing the concentration of bromine in the gas filter increases its transmission coefficient at 2850 A, thereby leading to a possible increase in the transmission of the combination light filter.

Apart from the light filter mentioned above, we also prepared a special monochromatic light filter which isolates only the resonance line of the mercury spectrum at 2537 A. This light filter was made from a crystal of KBr containing Tl and Pb and a crystal of KCl containing Pb. The gas filter was used as the supplementary filter. This light filter had a very narrow transmission band in the ultra-violet, the half width being only 20-30 A for a transmission coefficient of 4-5% at the maximum absorption band at 2535 A. If it is taken into account that this light filter is designed for the isolation of only the 2537 A line in the mercury spectrum and that this line makes up 30% of the intensity of all the spectrum of a mercury low pressure lamp, then the transmission of this filter will be adequate in a number of cases.

I should like to express my thanks to Prof. E.F.Gross, Corresponding Member of the Academy of Sciences of the USSR, for his constant interest in the work.

SUMMARY

In contrast to other absorbing light filters for the ultra-violet, crystalline light filters isolate a narrower spectral band with considerably less loss of light inside the transmission bands. In addition, the position of the transmission band itself can be shifted within limits along the spectrum by varying the proportions of the various components of a mixed crystal, whereby a light filter can be constructed for a chosen wave length and can be adjusted to suit actual experimental requirements.

The high transmission coefficient makes crystalline filters suitable both for investigating weak radiation as well as for getting optical images in ultra-violet light. It is evident that crystalline filters can be applied in many fields of scientific investigation; their stability to the effect of the ultra-violet, and also their constancy with time, enable crystalline light filters to be used in various types of optical apparatus.

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AN INVESTIGATION OF THE POSSIBILITY OF COLORIMETRIC ANALYSIS IN THE ULTRAVIOLET

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Contemporary colorimetry uses the absorption spectra of compounds which absorb in the 4000-7500 A region for analytical purposes. Accordingly, the colorimetric method of analysis can only be applied for the quantitative determination of intensely colored compounds and of compounds for which sufficiently selective color reactions can be chosen. At the same time, the exceptionally high sensitivity of colorimetric methods, and their fairly high selectivity, and the speed with which colorimetric determinations can be made, lead to a natural tendency to introduce colorimetric methods on an increasing scale into analytical practice.

A radical increase in the number of chemical compounds which can be analyzed by colorimetric methods can be achieved by using the ultraviolet for solving colorimetric problems. The use of absorption spectra in the near ultraviolet for the quantitative analysis of chemical compounds not only increases the number of substances which can be analyzed colorimetrically, but opens up new possibilities for colorimetric analysis without preliminary chemical treatment of the test material, by using the characteristic absorption of the test material. Application of the ultraviolet also enables more simple chemical reactions which lead to the formation of products absorbing in the ultraviolet to be used for the solution of colorimetric problems. The selectivity of the colorimetric determinations can also be considerably increased.

The number of investigations devoted to the study of the possibilities of colorimetric analysis in the ultraviolet is insignificant. The majority of them does not go beyond the construction of apparatus designed for production analysis of one compound, or at the best of a few chemical compounds [1-11]. It has been established thereby that a few substances can be determined colorimetrically by means of their characteristic absorption bands in the near ultraviolet, at concentrations of 10^{-6} to 10^{-7}%.

The main obstacle to the wide introduction to analytical chemistry of colorimetric methods based on absorption of ultraviolet radiation by compounds, is the absence of light filters for the 4000-2000 A region of the spectrum which can render the light monochromatic enough, and which possess stable spectral characteristics.

Glass of Types UFS [12], Corning [13-16], U.G. [17], isolate wide spectral bands in the ultraviolet, and do not ensure selective analysis. The small number of narrow band light filters for this part of the spectrum, which are constructed on the basis of the absorption of light by solutions [18-20], cannot be applied in colorimetry because of the variability of their spectral characteristics and their size. Heterogeneous ultraviolet light filters constructed on the principle of the selective scattering of light ensure highly monochromatic light beams, but the spectral results vary very considerably with temperature [21-23].

The problem facing colorimetry in the ultraviolet which logically arises from the huge mass of material which has been accumulated hitherto on the ultraviolet absorption spectra of chemical compounds and the small amount of study

devoted to this problem naturally necessitates further work on the potentially wide use of the ultraviolet in quantitative analysis. Accordingly, the work which we have carried out along these directions can be divided into three sections: a) development of the type of apparatus designed for colorimetric work in the ultraviolet; b) a search for chemical light filters which can monochromatize the ultraviolet sufficiently well and have stable spectral characteristics; c) determination of the sensitivity, accuracy, and reproducibility of the colorimetric determination of solutions of chemical compounds by their ultraviolet absorption spectra.

Apparatus

The apparatus proposed by us previously [24] was designed for objective colorimetry in the ultraviolet. The light flow was registered by means of two vacuum antimony-cesium photoelements prepared by the LIKI fitted into the arms of a photocolorimeter. The source of ultraviolet was a small hydrogen lamp with two-way radiation, made by the "Etalon" factory. The wattage of the lamp was 80-100, and it was supplied from 127 V a.c. mains (without voltage stabilization). The colorimeter lenses were made from crystalline quartz and the windows of the photoelements of Uviol glass.

The difference in the photo currents in the photoelement circuit was amplified by Krusser's method [25], which is exceptionally simple. The cells containing the solvent and the test solution respectively were placed in front of one of the photoelements, the second photoelement functioning as a balancing attachment. Readings are made by the method of optical compensations. The scatter in the readings of the transmission of the solutions does not exceed 0.5%.

Light Filters

a) Crystalline light filters. In choosing light filters for the range 2500-3000 A, we decided to use mixed crystals of the alkali-halide salts to which Pb^{2+} and Tl^{+} had been added.

The alkali halides in a crystalline state are transparent to the ultraviolet right up to 1800-2300 A [26, 27]; when small amounts of Pb and Tl are included in the crystals, it leads, as Hilsch [27] and Koch [28] have shown, to the appearance of intensive absorption bands in the 3100-2500 A region.

A comparison of the absorption spectra of aqueous solutions of salts of the type MeH (Me = metal, H = halogen) with additions of $PbCl_2$ and TlCl [29, 30] enables one to ascribe these absorption bands to complex compounds of the type TlH_x^{-x+1} and PbH_x^{-x+2}.

The spectral characteristics of mixed crystals were first used by Stekhanov [31] for preparing solid light filters having narrow transmission bands in the 2500-2850 A region.

The low values of the half-width of the transmission bands of Stekhanov's light filters (of the order of 80-200 A) and the stability of their spectral characteristics with time are strong reasons for using these filters in colorimetric analysis.

Using Stekhanov's data, but confining ourselves to investigating mixed crystals of the composition KCl + $PbCl_2$, KBr + $PbCl_2$, and KCl + KBr + $PbCl_2$, we established that the spectra of crystals of the type KCl + KBr + $PbCl_2$ cannot be regarded as a superposition of the absorption bands of the two first crystals - Figure 1. This fact favors both the view that the absorption of light is connected with the formation in the last case of complexes of the type $(PbCl_xBr_y)$, and also supports Sueda's hypothesis re the chromophoric properties of the trans groups of the form $H_1 - Me - H_2$ in the molecules of the complex compounds.

The mixed crystals of KCl + KBr + $PbCl_2$ were obtained by Kyropoylas' method [33] by growing them from a melt of the mixture of the salts on a primer fixed in the block of a water-cooled steel condenser.

By varying the composition of the mixture KCl + KBr + $PbCl_2$ we were able to supplement Stekhanov's results with the following three light filters:

1. Crystals of the composition KBr - 75%; KCl - 24.6%; $PbCl_2$ - 0.4%. Maximum transmission of the filter- λ_{max} = 270 mμ. For a crystal thickness of d = 3.5 mμ, transmission at the maximum was T_{max} = 55%, the half width of the transmission band was $\frac{\Delta\lambda}{2}$ = 200 A.

2. Crystals of the following composition; KBr - 20%; KCl - 79%; $PbCl_2$ - 1%. For d = 4 mm λ_{max} = 2600 Å; T_{max} - 50%; $\frac{\Delta\lambda}{2}$ = 150 A.

3. Crystals: 8% KBr + 90.8%; KCl + 1.2% $PbCl_2$. λ_{max} = 2570 A; for d = 2.5 mm; T_{max} = 70%; $\frac{\Delta\lambda}{2}$ = 230 A.

The crystals enumerated above, just like those prepared by Stekhanov, pass light of wave length 3200 A, which was then separated by Stekhanov by the use of Peskev's supplementary gas filters [3, 4], absorbing in the region 3200 to 5000 Å.

The gas filter is not suitable for colorimetric analysis, both because of its size and also because of its transparency to light of $\lambda > 5000$ A. Using Ottmer's data as a basis, we tried to replace the gas filter by a disc cut from a crystal of NaF which had been coated by heating in sodium or potassium vapor. However, as the amount of crystalline NaF at our disposal was limited, we, in parallel with Stekhanov, only carried out preliminary work on investigating a similar light filter, the spectral characteristic of which is given in Fig. 2. When working with a crystalline light filter of the composition given above we had to use, temporarily, a liquid light filter of the composition; 1.1 mol/liter Cl_2 + 0.24 mol/liter Br_2 in CCl_4. The thickness of the solution layer was 0.5 mm. One of the windows of the cell was made from UFS-1 glass, of d = 2mm. The spectral characteristic of this light filter is shown in Fig. 2, in comparison with the transmission curve for UFS-1 glass.

Crystals obtained in combination with such a filter are not transparent in the 3000 - 6700 A region; the maxima of their transmission curves lie at 2570, 2600 and 2700 A. The transmission at the maximum has values ranging from 100 to 15%. The half width of the transmission band is 80 to 160 A. The transmission curves are shown in Fig. 4.

b) Borate Glasses. In order to make light filters for the 3000 to 4000 region we made some experiments on the absorption spectra of borate glasses containing traces of heavy metals. These have not been studied in detail from an optical point of view. Some of the results obtained are given in Fig. 3.

The following light filters were prepared on the basis of similar glasses:

1) Glass of the composition: Na_2O — 30.7%; B_2O_3 — 69.1%; K_2CrO_4 — 0.2%. λ_{max} = 310 mμ; d = 1 mm; T_{max} = 15%, $\frac{\Delta\lambda}{2}$ = 18 mμ.

2) Glass of the composition: Na_2O — 30.75%; B_2O_3 — 69.14%; K_2CrO_4 — 0.1%; MnO — 0.001%. λ_{max} = 315 mμ; d = 1 mm; T_{max} = 18%; $\frac{\Delta\lambda}{2}$ = 20 mμ.

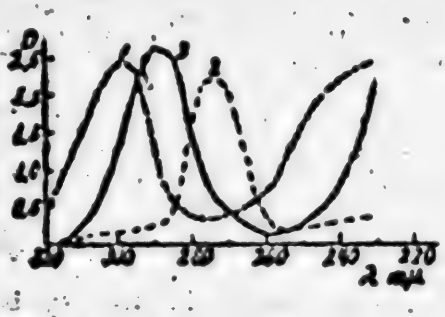

Fig. 1. Absorption curves for [illegible] crystals.
1) KBr + 0.[illegible] $PbCl_2$; 2) KCl + 0.[illegible] $PbCl_2$; 3) 50% KCl + 50% KBr + 0.[illegible] $PbCl_2$.

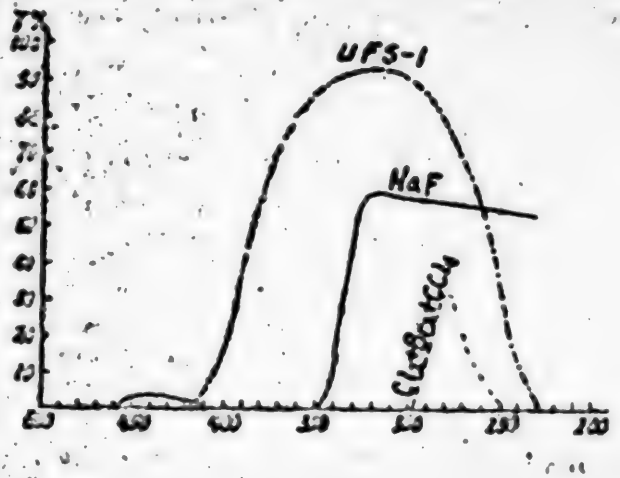

Fig. 2 Transmission curves

Glass UFS-1 (d = 2mm); crystal of NaF coated in Na vapor; liquid filter 1.1 mol/l Cl_2 + 0.14 mol/l Br_2 in CCl_4; (d = 0.5 mm)

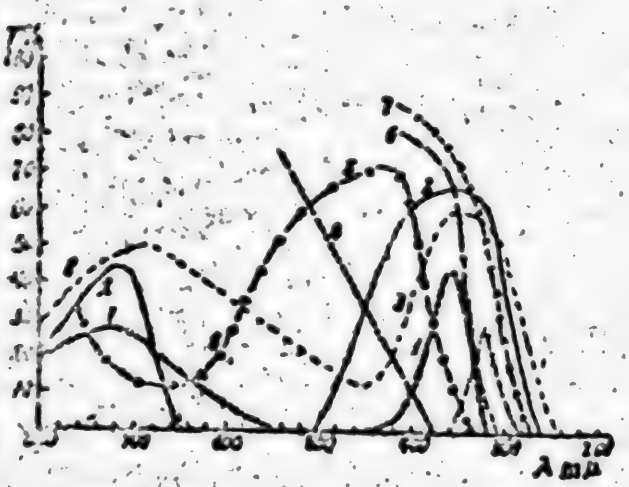

Fig. 3 Transmission curves for borate glasses

1 - Na_2O - 30.70%; B_2O_3 - 68.94%; MnO - 0.36%
2 - Na_2O - 30.66%; B_2O_3 - 68.87%; CoO - 0.47%; 3 - Na_2O - 30.7%; B_2O_3 - 68.9%; NiO - 0.4%; 4 - Na_2O - 30.78%; B_2O_3 - 69.17% K_2CrO_4 - 0.5%; 5 - Na_2O - 30.66%; B_2O_3 - 68.88%; CuO - 0.46%; 6 - Na_2O - 30.76%; B_2O_3; - 69.17%; FeO3 - 0.07%; 7 - Na_2O - 30.50%; B_2O_3 - 68.54%; PbO - 0.96%

3. Glass of the composition: Na_2O 30.72%; B_2O_3 69.01%; K_2CrO_4 0.1%; MnO 0.17%. λ_{max} = 320 mμ; T_{max} = 14%; $\Delta\lambda_{\frac{1}{2}}$ = 20 mμ.

4. Glass of the composition: Na_2O 30.67%; B_2O_3 68.92%; K_2CrO_4 0.07%; MnO 0.34%. λ_{max} = 330 mμ; d = 1 mm; T_{max} = 18%; $\Delta\lambda_{\frac{1}{2}}$ = 28 mμ.

5. Glass of the composition: Na_2O 29.98%; B_2O_3 68.02%; MnO 2%. Maximum transmission is located at λ = 355 mμ; d = 1 mm; T_{max} = 18-20%; $\Delta\lambda_{\frac{1}{2}}$ = 30 mμ.

The transmission curves for these light filters are given in Fig. 4.

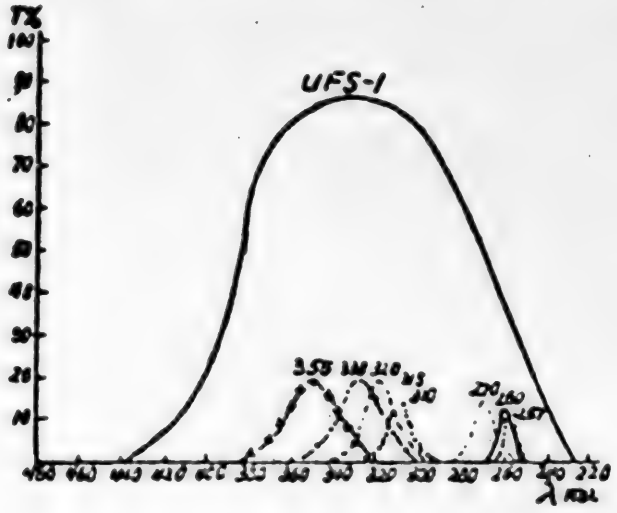

Fig. 4. Transmission curves for the light filters.

Colorimetric Determination in the Ultraviolet

The experiments which we carried out along this direction were not aimed at developing a method for the determination of any particular chemical compound, though the results given below could be used for a number of chemical analyses without essentially changing the colorimetric methods which we adopted. Any work on colorimetric analysis in the ultraviolet should evaluate the suitability of the apparatus and the light filters for carrying out analytical work in the spectral region 4000-2000 A, and also aim at determining the sensitivity and accuracy of such analysis. For this purpose, we chose some organic compounds suitable for colorimetric analysis, with intensive absorption bands in the ultraviolet, and also compounds having no absorption bands in the 2000-4000 A region. In the first case, which is the most suitable for colorimetric analysis, the determination is carried out directly with the help of the characteristic absorption of the substance, while in the second case a simple chemical reaction, in which the test compound is converted into a product which absorbs intensely in the ultraviolet, preceeds the colorimetric determination.

Benzene. The most sensitive method for the determination of benzene, which is based on the nitration to dinitrobenzene followed by colorimetric estimation of the latter in acetone solution with addition of alkali, enables quantitative analysis to be carried out right down to concentrations of benzene in the sample of the order of 10^{-4}% [36,37]. The experimental error amounts to 50%, and the analysis takes considerable time. We carried out colorimetric determinations of benzene in ethyl alcohol without any preliminary chemical treatment in a 5 cm cell with a light filter of λ_{max} = 260 mμ. Some of the analytical results, which are adduced in Table 1, demonstrate that even when working on the "edge" of the absorption band for benzene, i.e., at a known low sensitivity for colorimetric determination, it is still possible to determine the content of benzene in solution, down to concentrations of the order of 10^{-3}%, with reasonable accuracy.

Naphthalene. Methods for the quantitative determination of naphthalene which are based on its condensation with picric acid [38-39], on its nitration to nitronaphthalene or to trinitronaphthalene [40], and which are used for the analysis of coke-oven gas, for the analysis of air in factories, and in food products, enable it to be determined in amounts of 10^{-1} to 10^{-3}% in the test material. A long time is necessary for these analyses.

We made colorimetric determination of naphthalene solutions using a light filter with λ_{max} = 315 mμ, i.e., on the long wave side of the absorption band. The sensitivity of the analysis decreases with other filters, but benzene and its homologs do not interfere.

Results of the analysis carried out in a 5 cm cell are given in Table 2. The lower limit of the concentration, determined with a relative error of 6%, is ca. 10^{-4}%.

Anthracene. The most sensitive spectrophotometric method for the determination of anthracene in petroleum [41] allows it to be determined in concentrations of the order of 10^{-3}%.

TABLE 1

Benzene in Ethyl Alcohol

Benzene taken, in %	Benzene found, in %	Δc/c, %
0.050	0.047	6
0.040	0.041	2.5
0.030	0.032	7
0.021	0.022	5
0.015	0.016	6
0.010	0.010	0
0.0049	0.0047	6
0.0025	0.0023	8

TABLE 2

Naphthalene in Ether

Naphthalene taken, in %	Naphthalene found, in %	Δc/c, %
0.00075	0.00075	0
0.00068	0.00065	5
0.00060	0.00062	3
0.00050	0.00048	4
0.00045	0.00047	3
0.00040	0.00038	5
0.00023	0.00024	4
0.00017	0.00018	6

Results are given in Table 3 for the colorimetric determination of anthracene solutions using its characteristic absorption in the ultraviolet. The light filter used had λ_{max} = 355 mμ.

Nitrobenzene. By converting nitrobenzene into dinitrobenzene and carrying out a colorimetric analysis on the colored solution of the dinitrobenzene in acetone in the presence of alkali, it is possible to determine it quantitatively, at concentrations down to 10^{-4}%, with an error of up to 50% [36]. The method is not specific; benzene, toluene and xylene interfere.

In our experiments, the results of which are given in Table 3, we used the characteristic absorption of nitrobenzene in the ultraviolet. A light filter with λ_{max} = 315 mμ, i.e., outside the region of absorption by hydrocarbons of the benzene series, was used for the colorimetric determination. A determination takes 5-10 minutes, and the sensitivity is increased considerably.

Aniline. Small amounts of aniline are usually determined colorimetrically by means of the blue solutions which are formed by its oxidation with chloramine in the presence of phenol [36]. The lower limit of the concentration which can be determined quantitatively is of the order of 10^{-5}%. The error of the method amounts to 50% and ammonia and toluidine interfere.

It is possible to determine aniline colorimetrically with the same sensitivity, but with a smaller error, by its characteristic absorption in the ultraviolet.

Results of analysis which we carried out using a light filter with λ_{max} = 275 mμ for a cell length of 5 cm are given in Table 5.

Pyridine, quinoline. Colorimetric determinations of aqueous solutions of pyridine (Table 6), and of solutions of quinoline in ether (Table 7), using filters with λ_{max} = 260 mμ and λ_{max} = 315 mμ, demonstrated the possibility of determining both compounds quantitatively by means of their absorption spectra in the

ultraviolet at concentrations of the order of 10^{-4}%. The experimental error does not exceed 10-12%.

TABLE 3

Anthracene in Ether

Anthracene taken, in %	Anthracene found, in %	Δc/c, %
0.00017	0.00017	0
0.000113	0.000112	1
0.000050	0.000047	6
0.000034	0.000032	6
0.000020	0.000021	5
0.000015	0.000014	6
0.0000085	0.0000090	6
0.0000056	0.0000050	12

TABLE 4

Nitrobenzene in Ether

Nitrobenzene taken, in %	Nitrobenzene found, in %	Δc/c, %
0.00050	0.00048	4
0.00027	0.00026	4
0.00020	0.00019	5
0.00010	0.00011	10
0.00008	0.00008	0
0.00007	0.00007	0
0.000045	0.000040	11

TABLE 5

Aniline in Water

Aniline taken, in %	Aniline found, in %	Δ c/c, %
0.00125	0.00125	0
0.00055	0.00056	2
0.00040	0.00042	5
0.00023	0.00023	0
0.00015	0.00016	6
0.000080	0.000085	6
0.000059	0.000060	1.5
0.000050	0.000040	20

TABLE 6

Pyridine in Water

Pyridine taken, in %	Pyridine found, in %	Δc/c, %
0.0150	0.0145	3
0.0080	0.0084	5
0.0050	0.0049	2
0.0030	0.0030	0
0.00155	0.00150	3
0.00100	0.00102	2
0.00080	0.00075	7
0.00051	0.00045	12
0.00030	0.00032	7

TABLE 7

Quinoline in Ether

Quinoline taken, in %	Quinoline found, in %	Δc/c, %
0.00575	0.00580	1
0.00290	0.00280	3
0.00200	0.00200	0
0.00115	0.00110	5
0.00060	0.00063	5
0.00046	0.00043	7
0.00015	0.00018	20

TABLE 8

Carbon Disulfide in CH_4

Carbon disulfide taken, in %	Carbon disulfide found, in %	Δc/c, %
0.0183	0.0185	1
0.0075	0.0073	3
0.0044	0.0043	2.5
0.0026	0.0025	4
0.00101	0.00105	4
0.00069	0.00072	4
0.00050	0.00055	10
0.00040	0.00045	11

Carbon Disulfide. Small amounts of carbon disulfide are usually determined colorimetrically after conversion into colored copper dithiocarbamate. The sensitivity of such determinations amounts to 10^{-3}-10^{-4}% for a relative experimental error amounting to 50% [36].

We used its absorption of light of wave length 315 mμ for its determination. The results adduced in Table 8 indicate the high accuracy of this method. H_2S, which does not absorb in this spectral region, does not interfere.

Acetone, methylethylketone, and methylpropylketone. The lower limit of acetone concentration which can be determined by Messinger's method [42] is of the order of 10^{-3}%. The method based on the action of hydroxylamine hydrochloride on a sample containing the acetone, with subsequent titration of the HCl generated, has a similar sensitivity.

The absorption spectra of the aliphatic ketones include absorption bands at 270 mμ. The numerical values of the absorption coefficients, however, are insignificant, and enable ketones to be determined at concentrations of 10^{-2}% and higher in the test sample.

Messinger's reaction is characterized for aliphatic ketones of the type $CH_3 - CO - R$, whereby iodoform is obtained which has an exceptionally intense absorption band at 350 mμ. We used this fact as a basis for the colorimetric determination of small amounts of acetone, methylethylketone, and methylpropylketone.

20 cm^3 of a solution of the composition 200 g KI +100 g I_2 + 400 cm^3 water are measured into a 100 cm^3 separating funnel, and 6.6 cm^3 of 20% NaOH and 20 cm^3 of the solution to be tested for its ketone content added.

The mixture is shaken vigorously for 5 minutes, after which excess is destroyed by addition of 0.1 cm^3 of 5% $Na_2S_2O_3$, and the iodoform extracted with 20 cm^3 chloroform.

After 10 minutes standing, the chloroform is poured into the cell and the iodoform determined colorimetrically, using a light filter with λ_{max} = 355 mμ and a cell length of 5 cm.

The analytical results are given in Tables 9-11.

Aliphatic alcohols. Data on the sensitivities of various analytical determinations of small amounts of aliphatic alcohols are contradictory [38-44]. The lowest concentration which can be determined fairly accurately is ca. 10^{-3}%. Vorokhobin's method [45], when carefully followed, enabled the author to determine the concentration of ethanol in biological media down to concentrations of $5 \cdot 10^{-4}$% with an experimental error of the order of 10%.

Nizovkins's colorimetric method is complicated and leads to considerable loss of material [46].

For carrying out colorimetric determinations of solutions of methyl, ethyl, isopropyl, n-butyl and n-octylalcohols, we used the absorption spectra of the alkyl nitrites obtained by the action of nitrous acid on the respective solutions. These absorption bands occur at 370 mμ and 355 mμ. The procedure adopted was as follows; 20 cm^3 of the test solution, 1 cm^3 of 5N HCl, and 20 cm^3 of aviation gasoline [washed several times with H_2SO_4 (d = 1.84), NaOH solution and water] were placed in a 100-ml separating funnel, to which was quickly added 2 cm^3 of $NaNO_2$ solution, and the funnel shaken vigorously for 5 minutes. The gasoline layer was poured into a second separating funnel and shaken up with 20 cm^3 of 0.1 N NaOH for 5 minutes. The gasoline containing the alkyl nitrite was then poured into a 2 cm length cell and determined colorimetrically, using a light filter with λ_{max} = 355 mμ.

The results of these analyses are given in Tables 12-16.

SUMMARY

1. Using borate glass, ultraviolet light filters were made with maximum transmissions at 310, 315, 320, 330, and 355 mμ. In addition to Stekhanov's light

TABLE 9

Acetone in Water

Acetone taken, in %	Acetone found in %	Δc/c, %
0.00094	0.00093	1
0.00042	0.00041	2.5
0.00021	0.00020	5
0.00017	0.00018	6
0.000130	0.000125	4
0.000068	0.000070	3
0.000053	0.000050	6
0.000033	0.000035	8

TABLE 10

Methylethylketone in Water

Methylethyl-ketone taken, in %	Methylethyl-ketone found, in %	Δc/c, %
0.00067	0.00066	1.5
0.00040	0.00039	2.5
0.00034	0.00035	3
0.00025	0.00025	0
0.00018	0.00020	10
0.00010	0.00011	10
0.000065	0.000060	11
0.000032	0.000028	13

TABLE 11

Methylpropylketone in Water

Methylpropyl-ketone taken, in %	Methylpropyl-found, in %	Δc/c, %
0.00031	0.00030	3
0.00022	0.00021	5
0.00015	0.00015	
0.000110	0.000105	5
0.000095	0.000090	6
0.000075	0.000075	0
0.000040	0.000035	12
0.000018	0.000020	11

TABLE 12

Methyl alcohol in Water

Methyl alcohol taken, in %	Methyl alcohol found, in %	Δc/c, %
0.0200	0.0202	1
0.0116	0.0110	6
0.0085	0.0086	1.5
0.0058	0.0058	0
0.0046	0.0043	6
0.0030	0.0032	7
0.0022	0.0023	5
0.00085	0.00080	6

TABLE 13

Ethanol in Water

Ethanol taken, in %	Ethanol found, in %	Δc/c, %
0.0360	0.0354	2
0.0225	0.0224	0.5
0.0090	0.0096	7
0.0068	0.0064	6
0.0051	0.0051	0
0.0036	0.0040	10
0.0018	0.0020	10
0.0008	0.0007	12

TABLE 14

Isopropyl Alcohol

Isopropyl alcohol taken, in %	Isopropyl alcohol found, in %	Δ c/c, %
0.0375	0.0370	1.5
0.0100	0.0096	4
0.0066	0.0062	7
0.0042	0.0039	5
0.0020	0.0020	0
0.00125	0.00130	4
0.00080	0.00087	9
0.00040	0.00046	15

filters, crystal filters were also constructed which could isolate narrow parts of the spectrum at 257,260 and 270 mμ.

2. Using a number of organic compounds as examples, the possibility has been demonstrated of carrying out highly sensitive colorimetric determinations by means of the characteristic absorption of these compounds in the ultraviolet. In addition, it has been shown how it is possible to use simple chemical reactions

which give rise to the formation of products which absorb the ultraviolet intensely, for ultraviolet colorimetry.

TABLE 15

n-Butyl Alcohol

Alcohol taken, in %	Alcohol found, in %	Δc/c, %
0.0300	0.0293	2.5
0.0130	0.0135	4
0.0090	0.0092	2
0.0056	0.0054	4
0.0033	0.0030	10
0.0022	0.0024	9
0.0011	0.0013	18
0.00050	0.00058	16

TABLE 16

n-Octyl Alcohol

Alcohol taken, in %	Alcohol found, in %	Δc/c, %
0.0317	0.0320	1
0.0096	0.0090	7
0.0079	0.0082	4
0.0053	0.0048	9
0.0032	0.0032	0
0.0016	0.0015	6

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APPLICATION OF THE ULTRAVIOLET IN ANALYTICAL CHEMISTRY

3. A PHOTOMETER FOR ULTRAVIOLET COLORIMETRY

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The colorimeters and photometers which are in use at the present are adapted for working in the visible part of the spectrum, 750-400 mμ. For this purpose the following conditions must be satisfied:

1) the compound which is to be determined colorimetrically must be intensely colored;

2) the color of the compound must remain constant with time;

3) the solution which is to be analyzed colorimetrically should not contain colored compounds which can give rise to colors with the reagents.

These conditions are not always satisfied, so that the number of compounds which can be determined colorimetrically is restricted. The colorimetric determination of compounds having a yellow color or only very weakly colored is very difficult, while the colorimetric determination of colorless compounds is impossible.

By extending the spectral region used for colorimetry on the short wave length side, it becomes possible to increase the number of compounds which can be determined colorimetrically considerably.

By observations in the ultraviolet, it is often possible to use the absorption of rays by a complex of simple composition, or even of a simple compound which is colorless or only slightly colored in the visible part of the spectrum.

Some substances which interfere during colorimetric determinations by the normal method do not interfere in the ultraviolet, since their absorption spectra at certain wave lengths are characterized by a minimum absorption of the ultraviolet. Knowing the spectral characteristic of light absorption by solutions of various compounds, we can simplify the analysis considerably and reduce to a minimum the necessity of a preliminary separation of interfering elements.

If a cell containing a substance which absorbs the ultraviolet is placed in the path of ultraviolet rays, then on examining the cell through a fluorescent screen we see a weakening of the photoluminescence of the screen [1, 2]. If the test substance does not absorb the ultraviolet, then the photoluminescence of the screen remains unchanged. Thus, by having two fluroescent screens of equal intensity, we can estimate the extent of the absorption of the ultraviolet by the substance by placing the substance between the source of light and one of the screens, and examining the two screens simultaneously.

In the ultraviolet, in contrast to colorimetry in the visible spectrum, we are comparing not a characteristic color of the test solution, but the intensity of the photoluminescence of a screen, which is dependent on the extent of the absorption of light by the test substance in the given spectral region. Thus, we are rid of the necessity of satisfying certain conditions which must be observed in the visible spectrum.

On this principle of measuring the intensity of the photoluminescence according to the extent of the absorption of the ultraviolet by the test solution, a visual photometer has been constructed for the ultraviolet part of the spectrum.

The photometer proposed consists of the following basic parts: an ultraviolet source, an object stage with a quartz plane parallel cell, interchangeable objectives with fluorescent screens, and stands for carrying the photometric set-up.

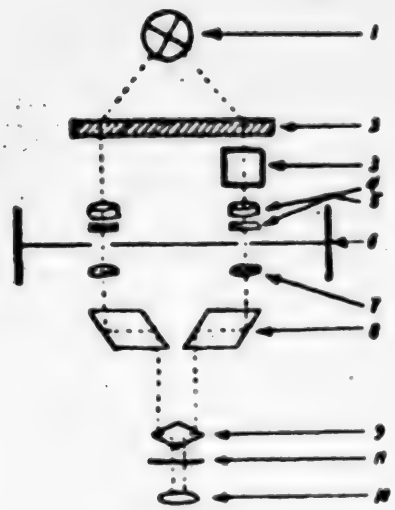

Fig.1. Schematic diagram of a photometer for colorimetry in the ultraviolet.

1) Light source; 2) and 11) light filters; 3) cell; 4) and 7) objectives; 5) florescent screens; 6) diaphragms; 8) and 9) prisms; 10) eyepiece.

The path which the rays follow and the experimental technique used for operating the ultraviolet photometer are clear from a consideration of the principal features of the set-up, as illustrated in Fig. 1.

The ultraviolet rays emitted by the light source 1, pass through a light filter 2, which removes the visible part of the spectrum from the radiation from the light source, leaving the part at 365-380 mμ. Subsequently, part of the ultraviolet rays falls directly on the objective of the photometric set-up 4, while the other part passes first through the cell containing a solution of the test material 3, and then on the objective 4. A layer of fluorescent material is superimposed on the back side of the objectives, which fluoresces only when ultraviolet light falls on it.

During the passage of the ultraviolet rays through the cell containing the test material, some of these are absorbed if the test material absorbs ultra violet-light of the given wave length, so that the photoluminescence of the objective will accordingly weaken more than the photoluminescence of the objective on which the ultra-violet rays fall directly.

In order to compare the intensities of the photoluminescence of the respective objectives, the apparatus is fitted with diaphragms 6, mounted on drums, and graduated in terms of the optical density of the solutions of the test material and the percentage transmission. Having passed through the diaphragms, the rays fall on the internal objectives 7, which serve as a control for ensuring that the rays are parallel, and then through the rhombic prisms 8, which bring the rays closer together. From the rhombic prisms the two sets of rays which have been brought close together fall on an acute-angled prism 9, which converges the rays closely so that the right-hand beam is visible in the eyepiece on the left-hand side of the illuminated field, while the left-hand beam is visible on the right-hand side of the eyepiece. From the acute-angled prism the rays fall on the eyepiece 10. Thus, in the eyepiece we can see two illuminated halves, which are not illuminated directly in the normal fashion from the source of light, but as a result of the photoluminescence of the screens.

If the test sample does not absorb the ultraviolet of a given wave length, then both halves of the field will be equally illuminated. If it does absorb,

then one half will be darker than the other. By rotating the drums attached to the stops, it is possible to equalize the intensities of the photoluminescences. The reading of the drum immediately gives the optical density and the amount of light transmitted, since the change in the amount of absorption of the ultraviolet rays of a given wave length by the substance is proportional to a change in the intensity of the photoluminescence.

Various regions of the ultraviolet spectrum can be chosen according to the absorption spectra of the test material. In order to do this the ultraviolet source can be changed. Thus, for the 365-380 mμ region the PRK-4 lamp or SVDSh-250 with UFS-3 light filters can be used; while for the 313 mμ region the PRK-4 with liquid light filters (a solution of potassium chromate in water) is suitable, and for the 254 mμ region, a bactericidal lamp fitted with a UFS-1 filter can be used.

When the region of the ultraviolet to be used is changed, the fluorescent screens must also be changed, since they are excited by lines of definite wave length in the ultraviolet.

In the set-up which we have adopted, we used screens excited by rays of wave length of ca. 365 mμ, consisting of ZnS·Cu, ZnS·Sb, Mn; and screens of uranium glass and $Ca_3(PO_4)_2$, F·Bi, Mn, for the 313 mμ region. Uranium glass can also be used for the ultraviolet region of 254 mμ.

When working in the 313 mμ region or in the shorter wave length regions of the ultraviolet, the fluorescent material is applied to the objective on the outer and not the inner side, since the glass of the objective completely absorbs ultraviolet rays of these wave lengths and no photoluminescence would be observed. When working in the 365 mμ region of the ultraviolet, the fluorescent material must be applied on the inner side of the objective in order that the monochromatic character of the excited photoluminescence be preserved (so that it should only be that from the 365 mμ region), since the fluorescent materials are excited by other regions to only a very insignificant extent.

The color of the photoluminescence will vary with the fluorescent material employed. It is best to choose fluorescent material which fluoresces with a white or a pale yellow color (the eye becomes less fatigued). A green light filter 11 may be introduced between the acute-angled prism 9 and the eyepiece 10, in order to increase the sensitivity.

The sensitivity of determinations carried out on our photometer exceeds that of visual measurements in the visible spectrum using the systems used at present in colorimeters and photometers, and is frequently equivalent to photoelectric methods. The mean sensitivity is 0.2-0.3 μg/ml.

As an example of the practical application of the photometer, we adduce below a method which we developed for the colorimetric determination of traces of iron in cobalt, using the photometer described above in the ultraviolet region.

The colorimetric determination of traces of iron in the presence of large amounts of cobalt is difficult in the visible spectrum because the measurements of the color intensity of the iron complexes must be carried out in the 430-450 mμ region, while in this region absorption bands of cobalt salts are also located (Fig. 2).

When iron is determined as the thiocyanate complex, the interfering action is even more strongly pronounced, because of the formation of a cobalt thiocyanate complex.

From the absorption curves it is clear that cobalt does not interfere with the determination of iron if light of wave length $\lambda = 365$ mμ is used, since these

rays are not absorbed by cobalt salts, while at the same time the absorption coefficient of the ferric thiocyanate complex remains high.

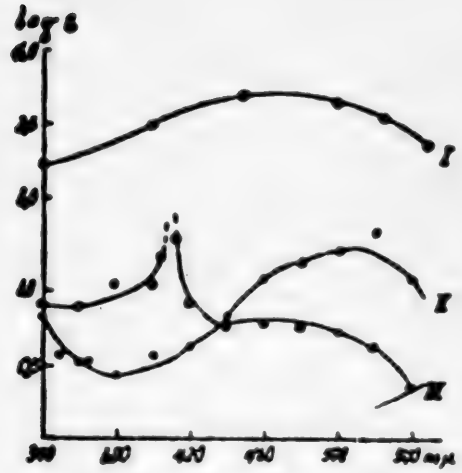

Fig.2. Absorption curves for solutions of ferric, cobalt and nickel thiocyanates. I) Fe^{3+} + CNS^-; II) Co^{2+} + CNS^-; III) Ni^{2+} + CNS^-

In order to determine iron in the presence of large quantities of cobalt, therefore, in this part of the spectrum we used the ultraviolet photometer described above.

The experimental procedure was as follows;

The test solution containing iron was placed in a 25 ml standard flask and acidified with 0.5 ml of HNO_3 (1:1); 2.5 ml of a 10% solution of potassium thiocyanate was then added, and the volume made up to the mark.

This solution was then transferred to the quartz plane parallel cell (25 ml capacity) in the ultraviolet photometer, and its optical density measured. Having measured the optical densities of a series of a series of solutions with varying iron concentrations, we constructed a calibration curve relating optical density (D) to iron concentration (Fig. 3).

Measurements carried out by means of the calibration curve showed that by means of this method it is possible to determine iron in amounts of from 0.005 to 0.2 mg in 25 ml with a relative error of 1-2% (Table 1).

Results for the determination of iron in solutions of its pure salts and in the presence of nickel and cobalt are given in Table 2.

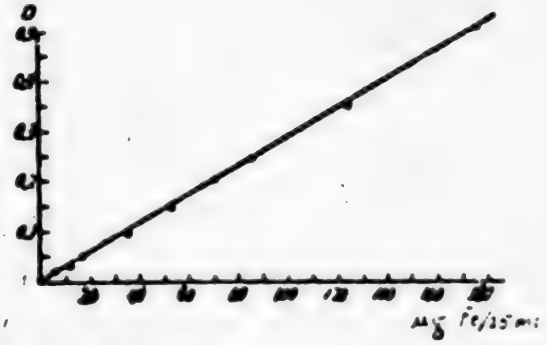

Fig.3. Calibration curve.

Cobalt does not interfere with the iron determination in amounts of up to 75μg per 25 ml solution. Nickel should not be present in amounts of more than 7.0μg per 25 ml.

The separation of iron from a solution containing cobalt and some nickel can be effected by coprecipitation of ferric hydroxide with the basic salts of these elements. For this purpose ammonia [1] is added to the weak acid solution of the elements till a small amount of precipitate is formed, which contains the basic salts of nickel and cobalt. The precipitate contains all the iron originally in solution (a colorimetric test on the filtrate for iron gave negative results).

1) The ammonia solution itself should not contain traces of iron. If it does, then a blank test must be made in which the iron is coprecipitated from the amount of ammonia to be used, by means of basic cobalt salts.

TABLE 1

Fe taken, in μg	Fe found, in μg	Relative error, in %
17.6	17.2	2.0
52.8	52.5	0.6
88.0	86.5	1.7

The filtrate is filtered off, washed with water, and washed from the filter paper into a beaker. The precipitate is then dissolved by an addition of 0.5 ml of HNO_3 (1:1). The solution obtained is transferred to a 25 ml standard flask and 2.5 ml of 10% potassium thiocyanate added; then it is made up to the mark with water. After mixing, the solution is transferred to the photometer cell and the optical density determined. From the calibration curve the concentration of iron which corresponds to the optical density determined for the solution can then be found.

TABLE 2

Fe taken, in μg	Co taken, in μg	Ni taken, in μg	Fe found, in μg	Relative error, in %
17.6	49.73	-	17.8	1.1
17.6	74.60	-	18.0	2.2
35.2	-	6.57	35.2	-
35.2	-	7.39	38.0	8.0
35.2	49.73	6.57	35.0	0.6

In conclusion we should like to express our deepest gratitude to Prof. Yu. V. Morachevsky for his advice in carrying out the work.

SUMMARY

1. The principles of colorimetry in the ultraviolet are described.

2. The construction of a photometer for ultraviolet colorimetry is described.

3. A method is described for the determination of traces of iron in cobalt by means of ultraviolet colorimetry.

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THE POLAROGRAPHY OF FUSED SALTS

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The nature of fused salts has attracted the attention of physical chemists and analysts for a long time. Practically all the methods of physico-chemical analysis have been widely applied for the study of fused salts. These include measurements of the electro-conductivity, viscosity, and electromotive force, etc. Nevertheless, none of these methods enables the presence of any particular ion to be established in the fused salts, or enables ionic processes occuring in the fused salts to be investigated. The attempts to use the polarographic method, which has found wide application for the study of solutions, for investigating fused salts are of particular interest. The American research workers Steinberg and Nachtrieb [1] mechanically carried over the practice of polarography with the mercury dropping electrode to the study of fused salts. Their work showed the limitations of polarography with the mercury dropping electrode. Only fused salts with temperatures not exceeding 180-200° can be investigated by this method. Considerable successes have been attained in the polarography of fused salts by the use of solid electrodes. In a number of researches which we carried out during 1947-1952 [2,3,4], we demonstrated the possibility of carrying out polarographic determinations on a number of cations, using fused salts as the supporting electrolytes, over the temperature range 200-1000°. Other authors [5,6] have confirmed our findings.

The fundamental question in the polarography of fused salts is that of the supporting electrolyte to be used. If one is to draw a complete analogy between the polarography of solutions and fused salts, one should select such a fused salt that it would by itself be a non-conductor for electricity, but by readily dissolving salts of the alkali metals it would become an electrical conductor. Of the inorganic salts, fused $ZnCl_2$, AlI_3 and certain others possess such properties. Thus, Izbekov and Nizhnik [6] obtained the following results for the electrical-conductivity in the system AlI_3 – KI:

% KI	0	1.58	3.68	7.78
χ in mhos	$2.34 \cdot 10^{-6}$	$5.52 \cdot 10^{-4}$	$2.68 \cdot 10^{-3}$	$8.42 \cdot 10^{-3}$

As can be seen, addition of KI leads to a sharp increase in the electrical conductivity of the fused salt. The use of $ZnCl_2$ as a supporting electrolyte for polarography has not been a success. Obviously as the result of the very slow removal of moisture from this salt when fused, its electrical conductivity is too high immediately after fusion without any KCl being added. In addition, because of the high viscosity of fused $ZnCl_2$, it is very difficult to handle. Further work should clarify the applicability of this salt as a suitable supporting electrolyte for polarographic work. Basically for the polarography of fused salts it is the easily-fusible alkali-metal salts which have been used, the cations of which are reduced at sufficiently negative potentials on a platinum electrode. The high electrical conductivity of these salts necessitates taking special precautions for suppressing condenser currents. Using these

salts as supporting electrolytes, it is possible to carry out polarographic determinations of ions reduced at potentials down to -10 V. Below this potential a general increase in the voltage-current curve of the supporting electrolyte occurs, and it becomes impossible to determine the wave height.

Ions in fused salts can be determined by means of various types of electrodes. Micro-electrodes, rotating electrodes, and the dipping electrode which we have suggested give equally good results. Micro-electrodes give small diffusion currents, so that at low concentrations determination becomes difficult. The rotating electrode gives considerably larger diffusion currents, but from the point of view of construction its application is very difficult. When working at high temperatures it is difficult to avoid vibrations of the electrode, which distort the polarographic process. Considerable difficulties also arise when changing the fused salts. In our opinion, the dipping electrode is the most suitable for studying the polarography of fused salts. Fundamental work has been carried out by means of this electrode, although both the micro-electrode and the rotating electrode have also been used for some determinations.

All these types of electrodes can be used for polarographic analysis by utilizing the following types of diffusion currents:

1) "throw" current, which is formed right at the very moment when the potential is applied;

2) "stable" current, established within 3-5 minutes after applying the potential;

3) polarographic current, formed for a definite rate of application of the potential.

The "throw" current corresponds to the smallest thickness of the diffusion layer, and has the greatest value. The "stable" current corresponds to the greatest thickness of the diffusion layer and has the least value. The polarographic current has an average value and its magnitude depends on the rate at which the potential is applied. For purely analytical purposes, the polarographic current is the most suitable. The "throw" and "stable" currents are of theoretical interest. In the majority of the cases cited below it was the polarographic current that was used.

Fused nitrates were first used as the supporting electrolytes for the polarographic determinations. The advantage of these as supporting electrolytes is the comparatively low fusion temperature; the eutectic ternary melt KNO_3-$NaNO_3$-$LiNO_3$ has a fusion temperature of about 140°. Its disadvantage is the ease with which the nitrates decompose at high temperatures. According to their behavior during polarographic determinations, all cations can be divided into three groups:

1) ions, the nitrates of which are stable at the temperature at which the analysis was carried out: Ag^+, Cd^{2+}, Pb^{2+};

2) ions, the nitrates of which are of low stability at the polarographic temperature: Cu^{2+}, Ni^{2+}, Co^{2+} and Hg^{2+};

3) ions, the nitrates of which are unstable: Fe^{3+}, Bi^{3+}, Mn^{2+}.

Ions of the first group give stable waves which remain practically unchanged during polarographic analysis. There is an essentially linear relation between the wave height and the concentration for a fairly large concentration range. The calibration curve for Ag^+ is given in Fig. 1. It is of interest to note that the polarographic waves obtained when various salts of a particular ion are introduced into the fused salts lie fairly close on one straight line. As an example, we give a calibration curve for Cd^{2+} which was obtained by the use of

different Cd salts. In addition, certain anions can be determined as well as cations when KNO_3 is used as the supporting electrolyte. In work carried out in conjunction with V.I.Kovalenko, the behavior of $Cr_2O_7^{2-}$ in fused KNO_3 was examined in detail. Just as for the cations, there is a linear relation between wave height and the concentration of $Cr_2O_7^{2-}$ (Fig. 3). In the course of 20-30 minutes after the addition of an aliquot of $K_2Cr_2O_7$ to the fused salt, the wave height remains almost unchanged: subsequently there is a gradual decrease as the result of a reduction process. The potentials at which ions of this group are deposited are given below.

Reduction potentials for ions using KNO_3 as supporting electrolyte and temperature of 260-280°

Ag^+ = -0.05 V; Pb^{2+} = -0.30 V;
Cu^{2+} = -0.42 V; $Cr_2O_7^{2-}$ = -0.40 V.

Determination of arbitrary amounts of the given ions by means of the calibration curves given above gave completely satisfactory results (Table 1).

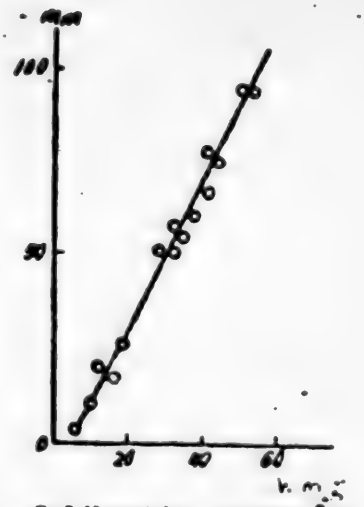

Fig. 1. Calibration curve for Ag ions using KNO_3 as the supporting electrolyte.

Ions of the second group give unstable waves which gradually decrease because of the decomposition of the nitrates according to the equation: $2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$.

The metal oxides thus formed are insoluble in KNO_3 and $NaNO_3$. For these ions, well defined polarographic waves, the height of which is proportional to concentration, are only obtained immediately after the addition of an aliquot of the respective salt to the melt. The stability of the polarographic wave can be increased by making the melts acid. If $KHSO_4$ is added to fused KNO_3 at 200-250°, then the nitrates of the ions belonging to this group will not decompose in this melt; the melt remains unchanged over a considerable time, and the wave height of the respective ions remains constant. When an acidic supporting electrolyte of this type is used, a straight line relation between wave height and concentration is found for Cu^{2+}, Ni^{2+}, Co^{2+} ions. A calibration curve for Cu^{2+} using an acidic nitrate melt as a supporting electrolyte is shown in Fig. 4 as an example. Hg^{2+} ions belong to this class of ions, which give unsteble waves. In this case, however, the instability of the wave is related to the sublimation of mercury salts at the high temperatures used. The reduction potentials of the ions of this groups are as follows.

Hg^{2+} = 0; Ni^{2+} = -0.65 V;
Cu^{2+} = 0.1 V; Co^{2+} = -1.0 V.

The cobalt ion is reduced at the point where there is an increase in the current, to which the supporting electrolyte itself gives rise, so that the Co waves can only be located with great difficulty.

There is a partial drop in wave height with time for $Cr_2O_7^{2-}$ also, this occurs because of the partial decomposition of KNO_3 with time at high temperatures, according to the equation: $2KNO_3 = 2KNO_2 + O_2$.

The NO_2^- ion thus formed then reduces the $Cr_2O_7^{2-}$ ions as described below, and the wave height for Cr_2O_7 drops.

To the ions of the third group belong those ions the nitrate salts of

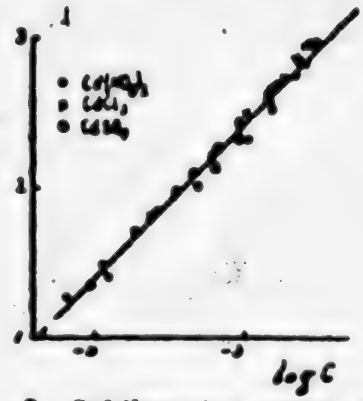

Fig. 2. Calibration curve for Cd^{2+} using KNO_3 as supporting electrolyte.

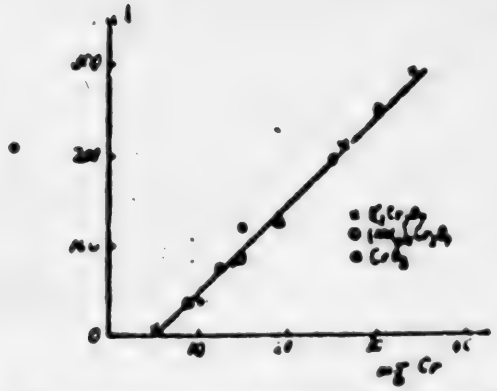

Fig. 3. Calibration curve for $Cr_2O_7^{2-}$ using KNO_3 as supporting electrolyte.

TABLE 1

Determination of Arbitrary Amounts of Salts

						Error, %
$AgNO_3$	Taken, mg	7	21	51.5		1.2
	Found, mg	7	22	53		
$Cd(NO_3)_2$	Taken, mg	42.5	72.5	91.5	98.5	2.6
	Found, mg	44	72.5	93	100	
$Pb(NO_3)_2$	Taken, mg	36	40 53	72	90	2.5
	Found, mg	38	43 56	75	90	
$K_2Cr_2O_7$	Taken, mg		88 132	290	396	4.0
	Found, mg		85 130	300	392	

TABLE 2

Reduction Potentials for Certain Ions, Using Chlorides as Supporting Electrolytes

Ion	Temperature, (°C)	Reduction potential (V)
Bi^{3+}	460	+0.55
Cu^{2+}	445	-0.08
Ag^{2+}	360	-0.15
Ni^{2+}	480	-0.50
Cd^{2+}	700	-0.55
Co^{2+}	450	-0.54

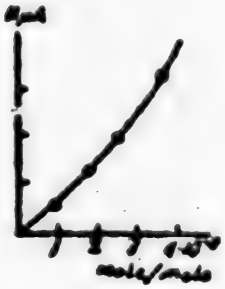

Fig. 4. Calibration curve for Cu^{2+}, using an acidic nitrate eutectic as supporting electrolyte.

Fig. 5. Current voltage curves and calibration curve for Ag, using a nitrate eutectic as supporting electrolyte, and a rotating electrode.

which decompose easily below the temperature at which polarographic determinations are carried out. These salts, on being introduced into the fused supporting electrolyte, immediately decompose with formation of the oxide of the

are carried out. These salts, on being introduced into the fused supporting electrolyte, immediately decompose with formation of the oxide of the respective metal, and no polarographic wave is obtained.

Similar results can be obtained by using the rotating electrode. A current-voltage curve for Ag which was taken using a rotating electrode in a supporting electrolyte of a low melting nitrate eutectic at 250° is given in Fig. 5. It is clear from these curves that a straight line relation exists between wave height and concentration.

The characteristic behavior of certain ions in a nitrate eutectic is worth noting. Despite the good solubility and stability of zinc salts, no waves could be obtained for zinc. This is connected with the very negative potential of zinc - below -1.0 V. The zinc wave coincides with the general increase in the current-voltage curve for the supporting electrolyte, and therefore cannot be determined. No waves were obtained for thallium either, because of the insolubility of TlCl in fused KNO_3. Of special interest is the behavior of potassium chromate in the supporting electrolyte. In spite of the complete solubility of this salt, no wave could be found for CrO_4^{2-} in the electrolyte. On increasing the temperature to 500-600° a wave characteristic of sexi-valent chromium appears. On adding ammonium chromate to the supporting electrolyte the wave of sexi-valent chromium appears even at 250-300°. This phenomenon is obviously connected with the fact that potassium chromate has a very high fusion temperature (t_{melt} = 975°), so that at the usual temperatures for polarography in fused salts it dissolves only very slightly into ions. $(NH_4)_2CrO_4$, on the other hand, decomposes even at 180°, and thereby forms chromic anhydride, which readily dissolves in KNO_3 and gives a well defined wave.

It was thus shown that polarographic determinations employing fused nitrates as supporting electrolytes are exclusively related to the stability of the respective salts at the temperature used. For the rest, from the analytical point of view there are no differences in principle between the polarography of solutions and that of fused salts.

Fused chlorides are more interesting than fused nitrates as supporting electrolytes. However, they do possess one disadvantage - a higher melting point. Even when fused chloride eutectics are employed, the temperature has to be kept at not less than 400-450°. Since the chlorides act as a neutral supporting electrolyte and are also more thermally stable than the nitrates, practically all the ions mentioned above can be successfully determined polarographically by means of fused chlorides as the supporting electrolyte. The only restriction is the reduction potential of the ion being determined. As indicated above, ions with reduction potentials below -1 V cannot be polarographically determined in fused salts because of the general increase in the voltage-current curve for the supporting electrolyte itself, which makes interpretations of the polarograms difficult. The reduction potentials of some ions using fused chlorides as supporting electrolyte are given in Table 2. The polarographic waves obtained when chlorides are used are more stable than those obtained using nitrates. Even on long standing the wave height remains unchanged. There is a straight line relation between wave height and concentration over a considerable concentration range. Determinations of arbitrary amounts of soluble ions by means of these straight lines give completely satisfactory results.

The mean error for a determinations is 3-4%. Copper and bismuth ions give good results during quantitative determinations. Copper salts are quite volatile when chlorides are used as supporting electrolyte, as a result of which the copper wave decreases fairly rapidly with time. Bismuth chloride contains a considerable amount of oxychloride, which is insoluble in the fused chlorides.

Fused silicates were also tried as supporting electrolytes. The characteristic features of this work on fused silicates were their high melting points and

TABLE 3

Determination of Arbitrary Amounts of Ni and Co Chlorides

$NiCl_2$	Taken, mg	95	153			
	Found, mg	90	148			
$CoCl_2$	Taken, mg	69	85	106	135	156
	Found, mg	73	92	104	136	157

their corrosiveness. The dipping electrode was used only with difficulty, because the porcelain and quartz tubes used for leading in the gas were very rapidly corroded by the melts, so that the polarographic relations were distorted. The micro electrode is the most convenient for working with fused silicates. As a result of the high electrical conductivity of the silicates themselves and of the insulation, large condenser currents appear on the polarograms and cannot be completely suppressed. The polarograms have a "creeping" character, and determination of the polarographic wave is very difficult. Despite this, a linear relation can be obtained between wave height and concentration for a number of ions. As an example the straight line obtained for fused copper oxide using a silicate melt as supporting electrolyte is given in Fig. 6.

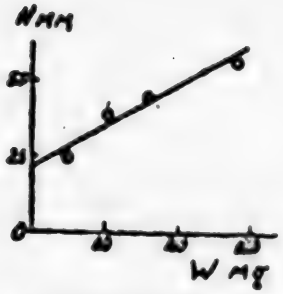

Fig. 6. Calibration curve for copper, using a silicate eutectic as supporting electrolyte.

As a result of the work carried out on the polarography of fused salts it can be seen that the polarographic determination of ions in solution in the fused salts is possible over the temperature range 180-1000°. The stability of the polarographic waves of the ions depends exclusively on the behavior of the test salt at the experimental temperature. Stable salts give well defined, stable, and easily reproducible waves. Volatile salts or ions giving unstable compounds with the supporting electrolyte give unstable waves which rapidly decrease with time. The chemical interaction between the supporting electrolyte and the ion to be determined, leading to the formation of products which are insoluble in the melt, can be prevented by making the melt acid. The order in which the ions are reduced remains basically the same as for solutions. For all the ions and for all the supporting electrolytes tested, a straight line relation was found to hold between the wave height and the concentration.

In addition to the polarographic determinations of ions, amperometric titration can also be applied for their determination in melts. Amperometric titration of ions in melts is carried out by the addition of micro amounts of the reagent which reacts with the ions to be determined. Precipitation, oxidation-reduction, and neutralization reactions, respectively, can be used for amperometric titrations just as in solution.

Precipitation reactions can be employed both for the determination of cations and anions. The alkali hydroxides can be used as universal reagents for the amperometric titrations of cations, using nitrates or chlorides as supporting electrolytes. On addition of NaOH or KOH to a melt containing some particular cation, the following reaction occurs:

$$Me(NO_3)_2 + 2KOH = MeO + 2KNO_3 + H_2O.$$

The metal oxides thus formed are insoluble in the fused chlorides or nitrates, and the wave height of the cation being determined falls. Titration can be carried out either by taking polarograms or by following the change in the diffusion current at constant potential. In the first case we get a straightened part for the equivalence point, while in the second case we get an ascending straight line. In both cases determination of the equivalence point is not difficult. This method of titration can be employed for investigating the $Cr_2O_7^{2-}$ ion by means of Ba^{2+}. The $BaCrO_4$ formed is insoluble in the fused nitrate, and the $Cr_2O_7^{2-}$ wave gradually falls. Results of titration by the precipitation method are completely satisfactory.

As an example of amperometric titration in which an oxidation-reduction reaction occuring in the melt is used as a basis, we adduce the titration of $Cr_2O_7^{2-}$ with micro amounts of $NaNO_2$, using KNO_3 as supporting electrolyte. During titration the following reaction takes place:

$$K_2Cr_2O_7 + 6NaNO_2 = 2KCrO_2 + 6NO_2 + 3Na_2O,$$

as a result of which the $Cr_2O_7^{2-}$ wave falls (Fig. 7). Determination of the equivalence point is not difficult. Titrations of arbitrary amounts of the ion to be determined, either by a precipitation reaction or by an oxidation-reduction reaction, give good results, as shown in Table 4.

TABLE 4

Determination of Arbitrary Amounts of Various Salts by Amperometric Titration

Salts	Supporting electrolyte	Result of titration					
$AgNo_3$	KNO_3	Taken, mg	53	74	75	123	144
		Found, mg	52	74	72	123	143
$CdCl_2$	KNO_3	Taken, mg	40	107	113		
		Found, mg	41	109	116		
$Pb(NO_3)_2$	KNO_3	Taken, mg	36	40	72	90	105
		Found, mg	38	43	75	90	104
$NiCl_2$	KCl + LiCl	Taken, mg	68	152	190		
		Found, mg	65	156	192		

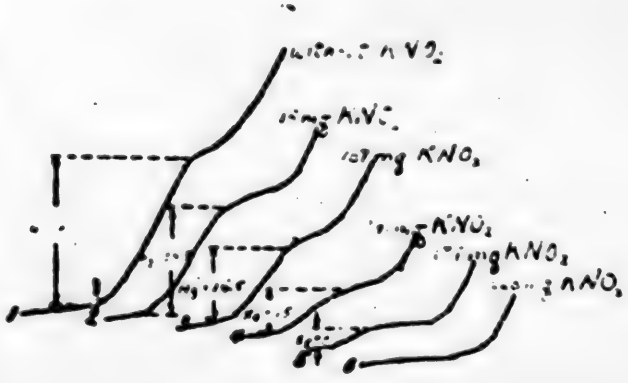

Fig. 7. Current-voltage curves for the titration of $Cr_2O_7^{2-}$ with micro-quantities of KNO_2.

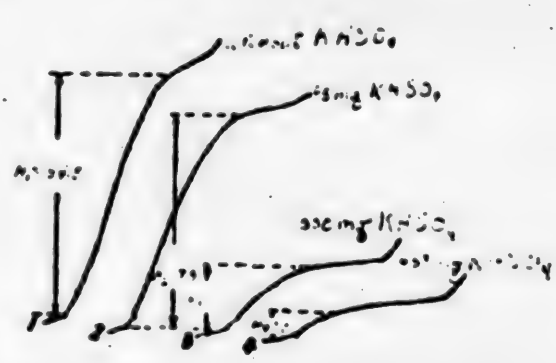

Fig. 8 Current-voltage curves for the titration of OH^- with micro-quantities of $KHSO_4$.

Amperometric titration can also be carried out on the basis of neutralization reactions. On adding alkali to a neutral melt of KNO_3 or KCl, a wave given by the hydroxyl ions is obtained, which is located at positive potentials. On adding micro amounts of $KHSO_4$ to such a fused mixture, the OH^- wave gradually decreases. The amperometric curve for such a titration is given in Fig. 8. Determination of the equivalence point is not difficult. It should be noted, however, that the concept of the precipitant for ions in solution is not the same as the concept of a precipitant for melts. Thus, in fused KNO_3, the Ag^+ ion cannot be titrated with KCl, since the AgCl dissolves readily in fused KNO_3, and no decrease in the wave height occurs. In exactly the same way the $Cr_2O_7^{2-}$ wave is not depressed on addition of Pb^{2+} to the melt. In fused silicates, amperometric titrations of cations with the universal reagent KOH cannot be carried out because the metal oxides so formed dissolve readily in the fused silicates, and free metal ions which are reduced on the solid electrode remain in the fused silicates.

The polarographic method of analyzing fused salts has great possibilities. By means of this method it is possible to follow changes in ionic concentrations which occur in the fused state. It can also be used for solving a number of physico-chemical problems relating to processes occuring in melts, the study of equilibrium between metal and melt, etc.. Of particular interest is the application of this method for investigating fused silicates, whose nature is of interest to metallurgists and geologists.

SUMMARY

1. The polarographic method of analysis using solid electrodes is a very promising method for the study of fused salts.

2. The possibility of determining a particular ion in a melt is determined fundamentally by the stability of the salt of the ion being determined polarographically at the experimental temperature.

3. The stability of a melt can be increased by making it acid by addition of $KHSO_4$.

4. Essentially linear relations were found between the wave height and concentration for the majority of ions studied.

5. Determinations of arbitrary amounts of various ions gave completely satisfactory results – the experimental error being 3-4%.

6. The concentrations of ions in melts can be determined by amperometric titration using precipitation, oxidation-reduction, and neutralization methods. Determinations of arbitrary amounts give results with errors of 3-4%.

7. The nitrates, chlorides, or silicates of the alkali metals can be used as supporting electrolytes for polarographic determinations.

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PHYSICO-CHEMICAL METHODS OF ESTIMATING ANTIBIOTICS

A COLORIMETRIC METHOD FOR THE QUANTITATIVE DETERMINATION OF STREPTOMYCIN

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The majority of chemical methods for the determination of streptomycin are based on characteristic reactions of the various functional groups in its molecule.

Thus, reactions of the carbonyl group of the streptomycin molecule are used as well as those of the guanidine group of the streptide part, and of the maltol formed from the streptose part on alkaline hydrolysis [1].

In view of the fact that preparations of streptomycin in a number of cases contain biologically inactive products of its decomposition which contain just these functional groups, and also a number of other contaminants with similar groups, the specificity of any analytical method which makes possible the determination of streptomycin alone in the presence of its decomposition products becomes of primary importance.

The simultaneous presence of guanidine and carbonyl groups in substances of biological origin is fairly rare, and the co-existence of these groups in the streptomycin molecule can therefore be used for analytical purposes. E.g., in the acridylhydrazine method of determining streptomycin, the specific properties of fluorescent streptomycin acridylhydrazine are used for its isolation from other hydrazones [2].

We have worked out a colorimetric method for the determination of streptomycin, based on the specific properties of the colored substituted hydrazone of streptomycin. As reagent we employed 2,4-dinitrophenylhydrazine, which is very widely used as a reagent in organic chemistry.

It should be noted that the given method, just like those mentioned above, is a method which determines total streptomycin and mannoside streptomycin – a substance which usually accompanies streptomycin, and which differs from streptomycin only in the presence of the d-mannose residue in the N-methyl-l-glycosamine part of the molecule. For the sake of brevity, we shall not stipulate again that in the presence of mannoside-streptomycin, both components must be determined.

During the reaction between streptomycin and 2,4-dinitrophenylhydrazine in acid media, the 2,4-dinitrophenylhydrazone of streptomycin is formed.

Excess of the colored reagent is extracted with butyl acetate. The streptomycin hydrazone remaining in the aqueous phase is colored yellow in acid solution, and the optical density D in the absorption band of the solution at $\lambda = 4300$ Å is a function of the streptomycin concentration.

Using highly purified streptomycin, a calibration curve D, c was constructed, and the concentration of test solutions determined by means of it. By making up synthetic mixtures of highly purified streptomycin and glucosamine, and of streptomycin and various sugars, we showed that sugar and amino sugars do not interfere with the determination of streptomycin.

The advantage of the dinitrophenylhydrazone method is its high specificity,

which enables it to be used not only for marketed streptomycin preparations, but also for the semi-products of production right up to the liquid culture stage.

EXPERIMENTAL

Two variants of the method are proposed.

First Variant. 10 ml of the solution containing streptomycin, in concentrations of from 20-120 µg/ml is introduced into a 15-20 ml test tube fitted with a ground glass stopper, and 0.5 ml of 2,4-dinitrophenylhydrazine reagent added. This reagent is prepared as follows: to 0.2 g of 2,4-dinitrophenylhydrazine - "State Chemical Reagent Purity" - are added 1 ml of concentrated sulfuric acid, 1.5 ml water, and 5 ml of rectified alcohol, and the solution thus obtained filtered if it is turbid. Fresh solution is prepared daily.

The ground glass stopper is inserted in the test tube, which is stood for 2.5 minutes in a boiling water bath; it is then removed and cooled with water. The solution is then extracted four times with approximately 10-ml portions of butyl acetate. The butyl acetate is used several times; it is purified by normal distillation. After the fourth extraction of the water phase, which is colored yellow if streptomycin hydrazone is present, it is allowed to stand, and the volume of the solution necessary to fill a 10 mm long cell taken out with a pipet. The optical density for the absorption band of the given solution λ = 4300 A is then measured on a differential photoelectric colorimeter.

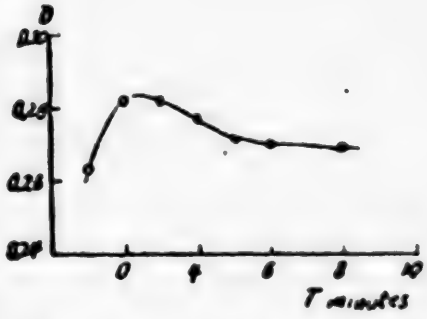

Fig.1. Relation between optical density D and the length of time for which the solutions of streptomycin and dinitrophenylhydrazine are boiled.

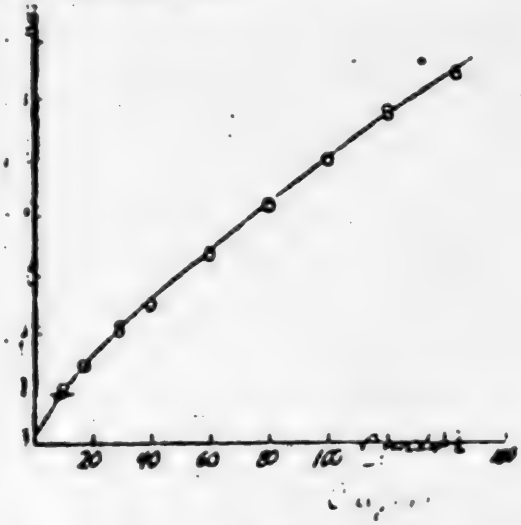

Fig.2. Calibration curve characterizing the relation between the optical density D of streptomycin hydrazone solution and the original concentration c of the streptomycin.

When the dinitrophenylhydrazine method was carried out using water instead of the original streptomycin solution, the optical density of the aqueous phase after extraction with butyl acetate proved to be zero. We therefore used water as a comparison solution.

We studied the relation between the time of heating of the solution of streptomycin and dinitrophenylhydrazine on the optical density of the solution of streptomycin hydrazone (for λ = 4300 A).

From Fig.1, it is clear that the maximum optical density is obtained for the hydrazone solution for a heating time of 2-3 minutes; we therefore chose a heating time of 2.5 minutes.

The calibration curve characterizing the relation between optical density D and the streptomycin concentration c was constructed, using the highly purified crystalline double salt of streptomycin hydrochloride and calcium chloride, with a known weight of streptomycin as the base.

Second Variant. Streptomycin dinitrophenylhydrazone can be formed at room temperatures and not just by boiling; at room temperature, however, the reaction is considerably slower. We determined the relation between optical density of aqueous solutions of streptomycin hydrazone and the time of standing of the solution of streptomycin plus dinitrophenylhydrazine at room temperature (Fig. 3).

It is clear from Fig. 3 that after two hours the optical density remains practically constant.

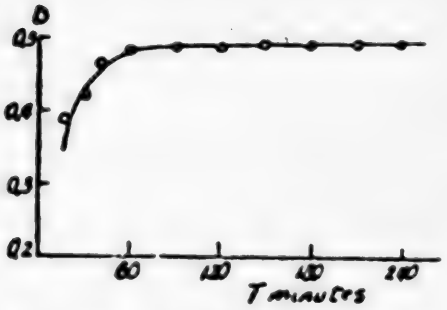

Fig. 3. Effect of time of standing of solutions of streptomycin plus dinitrophenylhydrazine on the optical density of streptomycin - hydrazone solutions.

On this basis the procedure adopted for the determination of streptomycin at room temperatures is as follows: 10 ml of the original streptomycin solution is transferred to a 50-100 ml separating funnel, and 0.5 ml of the 2,4-dinitrophenylhydrazine reagent added. The solutions are well mixed and allowed to stand for 2 hours at room temperature. The solution is then extracted four times with butyl acetate, as for Variant I. A calibration curve is constructed in the same way for this variant.

The minimum concentration of streptomycin which can be determined (for both variants) using a 10 mm cell amounts to 15-20 μg/ml. The concentration can be lowered considerably by increasing the cell length. When a cell 40 mm long was used, it was possible to determine a streptomycin concentration of 5 μg/ml.

Both variants have a high reproducibility. The deviation between individual determinations does not exceed 2%. Determinations of streptomycin in the same sample using the two variants give the same results.

When streptomycin was determined in purified samples by the dinitrophenylhydrazone and maltol methods, coincident results were obtained. The advantage of the dinitrophenylhydrazone method as compared with the maltol method is its higher sensitivity (approximately 4-5 times).

We carried out determinations of the streptomycin content of samples of varying degrees of purity. When the streptomycin was determined in the liquid culture, protein was first of all precipitated and the culture clarified.

In order to remove proteins, we used a 15% solution of trichloracetic acid, an amount of acid being added such that its concentration in the liquid culture was finally 3%. The precipitated protein was removed by centrifuging, while the excess trichloracetic acid was extracted with benzyl alcohol [3].

The culture liquid was clarified by shaking it with 0.5% activated charcoal (calculated on the volume of the liquid) in a strongly acid medium (pH 1.5-2).

We established that at such a pH no inactivation of the streptomycin occurred in the course of 1-2 hours.

Under these conditions streptomycin is not adsorbed by the charcoal and

remains completely in solution. Streptomycin can then be determined in the purified liquid culture by the usual dinitrophenylhydrazine method.

In the absence of, or for low contents of mannozostreptomycin as determined by the anthrone method [4], the streptomycin content of a sample coincides with the microbiological action of the preparation (Vide Table).

Comparison of Streptomycin Content as Determined by the Dinitrophenylhydrazine Method and From its Microbiological Activity
(streptomycin content assumed to be 100%)

No.	Preparation	Microbiological activity, in %	Deviation between chemical and microbiological methods, in %
1	Marketed product	106	+6
2	Marketed product	103	+3
3	Marketed product	101	+1
4	Concentrate	99	-1
5	Concentrate	99	-1
6	Eluate	87	-13
7	Eluate	92	-8
8	Liquid culture	100	-0

SUMMARY

A colorimetric method has been developed for the determination of streptomycin (two variants) which has high specificity and sensitivity. By means of this method it is possible to determine streptomycin both in marketed streptomycin and in the semi-products of production right up to the liquid culture stage.

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THE SECONDARY ADSORPTION OF IONS ON ALUMINUM OXIDE ALUMINATE

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The formation of chromatograms of ions on aluminum oxide can be brought about by the following processes:

1) by adsorption of the potential-determining ions;

2) by molecular adsorption of the electrolyte;

3) by exchange adsorption of the ions; and

4) by the precipitation of a difficultly soluble precipitate.

Ion-chromatograms on aluminum oxide aluminates [1] belong predominantly to the exchange type of chromatograms [2]. The formation of cation chromatograms on cation exchange aluminum oxide occurs as a consequence of the exchange of the cations of a solution for sodium ions [3]:

$$(Al_2O_3)_m\ AlO_2^-\ Na^+ + MZ \rightleftarrows (Al_2O_3)_m\ AlO_2^-\ M^+ + NaZ\ .$$

During the adsorption of cations on chromatographically active aluminum oxide, Schwab and coworkers discovered the phenomenon of joint adsorption of anions with multivalent cations. This phenomenon was not explained by the authors; neither was the absence of anion adsorption in the case of univalent cations taken into account.

If this fact is taken into account, the joint adsorption of anions and multivalent cations [3] can be explained as follows; part of the cations M^{2+} is exchanged with the sodium ions of the aluminum oxide aluminate, according to the scheme:

$$(Al_2O_3)_m \begin{matrix} AlO_2^- & Na^+ \\ AlO_2^- & Na^+ \end{matrix} + MZ_2 \rightleftarrows (Al_2O_3)_m \begin{matrix} AlO_2^- & \\ AlO_2^- & M^{2+} \end{matrix} + 2NaZ\ ,$$

while part of the cations will supercharge the aluminum oxide:

$$(Al_2O_3)_m \begin{matrix} AlO_2^- & Na^+ \\ AlO_2^- & Na^+ \end{matrix} + \begin{matrix} MZ_2 \\ MZ_2 \end{matrix} \rightleftarrows (Al_2O_3)_m \begin{matrix} AlO_2^- & M^{2+} & Z^- \\ AlO_2^- & M^{2+} & Z^- \end{matrix} + 2NaZ\ .$$

On the $AlO_2^-\ M^{2+}\ Z^-$ parts, exchange of anions occurs, while the joint adsorption of anions proceeds in parallel with their absorbability on the anion exchange aluminum oxide.

During the study of the chromatographic separation of anions on anion exchange aluminum oxide aluminate, we discovered the phenomenon of the joint adsorption of cations with multivalent anions. No secondary adsorption of cations was observed in the chromatography of univalent anions.

1) Deceased.

By analogy with chromatography on the cation exchange aluminum oxide, the joint adsorption of cations M^+ with multivalent anions Z^{2-} on the anion exchange aluminum oxide proceeds as follows:

$$(Al_2O_3)_m \begin{matrix} AlO^+ \\ AlO^+ \end{matrix} \begin{matrix} NO_3^- \\ NO_3^- \end{matrix} + ZM_2 \rightleftarrows (Al_2O_3)_m \begin{matrix} AlO^+ \\ AlO^+ \end{matrix} \begin{matrix} Z^{2-} \\ Z^{2-} \end{matrix} \begin{matrix} M^+ \\ M^+ \end{matrix} + 2MNO_3,$$

part of the anions is exchanged for the NO_3^- group as usual:

$$(Al_2O_3)_m \begin{matrix} AlO^+ \\ AlO^+ \end{matrix} \begin{matrix} NO_3^- \\ NO_3^- \end{matrix} + ZM_2 \rightleftarrows (Al_2O_3)_m \begin{matrix} AlO^+ \\ AlO^+ \end{matrix} Z^{2-} + 2MNO_3$$

Consequently, the formation of secondary exchange chromatograms on anion exchange aluminum oxide is possible.

A Description Of Secondary Cation Exchange Chromatograms

Chromatographic tubes of internal diameter 0.6-1.0 cm were used for the work. Aluminum oxide aluminate was introduced into the tube in the form of a suspension in 1 N HNO_3, the column being subsequently washed with water and a solution of a mixture of 1 N salts of various elements.

1. $CuSO_4 + Cu(NO_3)_2$

The column is colored blue by the copper ions. On washing with water the lower part of the blue zone becomes white. After development with an ammonium sulfide solution the black color of the cupric sulfide only appears in the upper part of the column at the point where the blue zone was not washed with water. In accordance with the adsorption series of the anions on the anion exchange aluminum oxide [1], the SO_4^{2-} anions are found higher than the NO_3^- ions in the columns. As a result the copper ions are adsorbed only by the bivalent SO_4^{2-} ion on the anion exchange aluminum oxide; they are not adsorbed in the zone of the univalent anions of NO_3^-.

2. $NiSO_4 + Co(NO_3)_2$

Initially a rose color appears which, in accordance with the extent of washing with water, disappears. On developing with ammonium sulfide, a black zone of cobalt sulfide only appears in the upper part of the column, which indicates that the cobalt ions are only adsorbed by SO_4 ions.

3. $NiSO_4 + NiCl_2$

Initially the column is colored green by nickel ions, subsequently, on washing with water, the column becomes white. Development with ammonium sulfide shows up a black zone of nickel sulfide in the upper part of the column.

4. $UO_2(NO_3)_2 + K_2SO_4$

The column is colored yellow by uranyl ions. After washing with water the yellow color disappears, but on development with potassium ferrocyanide a red color of uranyl ferrocyanide appears.

5. $Cr_2(SO_4)_3 + UO_2(NO_3)_2 + K_2SO_4$

K_2SO_4 is added in order to increase the concentration of the sulfate ions

in the solution. At the top of the column the grey-green color of chromium ions appears, while below the yellow color of the uranyl ions develops. On washing with water the gray-green color remains, while the yellow disappears, but on development with potassium ferrocyanide a red zone of uranyl ferrocyanide can be detected in the lower part.

6. $UO_2(NO_3)_2 + K_2SO_4 + CuSO_4$.

On the top a yellow zone of uranyl ions is obtained, while below the blue zone copper appears. On washing with water the yellow color disappears while the blue remains, though it gets paler. Development with ammonium sulfide gives in the upper part a brown zone of uranyl sulfide, while the bottom part becomes black with cupric sulfide.

7. $Cr_2(SO_4)_3 + CuSO_4$.

The upper part acquires the grey-green color of the chromium ions, the middle is a mixed zone, and the lower zone is blue as a result of adsorption of the copper ions. Separation of the cations is incomplete, but Cr^{3+} and Cu^{2+} form a partially mixed zone on the cation exchange column of aluminum oxide.

8. $CuSO_4 + CoSO_4$.

Two zones are formed; a blue copper zone on top and a rose cobalt zone below.

9. $CuSO_4 + NiSO_4$.

On top the blue copper zone develops, and below the green zone of nickel. On washing with water both zones become paler, particularly the nickel zone. Development with dimethylglyoxime gives a red color in the nickel zone.

10. $CoSO_4 + NiSO_4$.

One mixed zone is formed; Co^{2+} and Ni^{2+} also form a mixed zone on cation exchange aluminum oxide.

These experiments show that the formation of secondary cation exchange chromatograms on anion exchange aluminum oxide proceeds in parallel with their adsorbability on the cation exchange aluminum oxide, in the order

$$Cr^{3+} > UO_2^{2+} > Cu^{2+} > Co^{2+}, Ni^{2+}$$

(the ions separated by the comma form a mixed zone)

In conclusion, we note that when carrying out chromatographic adsorption of solutions of electrolytes it is essential to bear in mind the fact that secondary adsorption of two oppositely charged ions occurs if the adsorbed ions are multivalent.

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A VOLUMETRIC METHOD FOR THE DETERMINATION OF POTASSIUM

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In most cases potassium has to be determined in the presence of sodium, and sometimes in the presence of lithium and magnesium as well.

There are two basic methods for the determination of potassium in presence of sodium, viz., the chloroplatinate and the perchlorate methods. Both methods require a comparatively long time and require reagents which are not always readily available, or are expensive. Hitherto, no other accurate methods for the determination of potassium in the presence of sodium have been available.

Many variants of the method for the determination of potassium as the cobaltinitrite have been suggested. The chief defect of this method is that the precipitate of potassium cobaltinitrite, to which the formula $K_2Na[Co(NO_2)_6]\cdot H_2O$ is ascribed, does not always have this composition [2].

The aim of the present work was the development of a simple and rapid volumetric method for the determination of potassium, in which it is given a preliminary precipitation as potassium bitartrate. The bitartrate method is known in many variants but most research workers consider it to be insufficiently accurate. As far as accuracy is concerned it seems to us that Daubner's method [3] is the most suitable. In this method potassium is precipitated by a reagent containing 20 g of tartaric acid and 5 g sodium acetate in 1 liter of 50% aqueous alcohol.

On precipitation of the potassium bitartrate, the freed mineral acid which is formed in solution colors methyl orange a red color: $KCl + H_2C_4H_4O_6 \rightarrow KHC_4H_4O_6 + HCl$. According to Daubner's procedure the reagent is added until the color changes from orange to yellow. Excess of reagent should not be used, as it leads to high results.

On using the method as such, it proved to be extremely difficult to determine the necessary amount of reagent, since the change in color of the indicator for a given reagent composition is practically unobservable.

The change in color of the indicator can be made more clear cut if the ratio of tartaric acid to sodium acetate in the reagent be changed, the amount of the sodium acetate being increased. A reagent of such a composition, however, on standing deposits sodium bitartrate crystals in the form of long needles.

Another defect of this method is that sodium is introduced into the mixture being analyzed, in the reagent. This is of importance in those cases where the potassium content of a test sample is high and the determination of sodium by the uranyl acetate method is only possible after removal of the potassium [4].

We have shown that potassium can be precipitated by aniline or pyridine tartrate so that no sodium need be added. The amount of reagent necessary to precipitate the potassium is determined by the change in color of methyl orange from red to yellow. Sodium, lithium and magnesium in the form of chlorides, sulfates, or nitrates do not interfere.

To the test solution containing ca. 5 mg of K/ml, sufficient alcohol is added (methyl or ethyl) so that its final concentration in the solution is 50%. The reagent for precipitating potassium is prepared by dissolving 20 g of tartaric acid in 500 ml of water and adding 8 g of freshly distilled aniline (or 7 g of freshly distilled pyridine), and diluting to 1 liter with alcohol. The reagent is added dropwise, while the solution is continuously mixed with a glass rod. When the potassium starts to precipitate, the solution which contains methyl orange as the indicator is colored red. Mixing is continued, and more reagent added dropwise until the color of the indicator changes to yellow and does not change on adding more reagent. The potassium bitartrate which precipitates is allowed to stand for 2 hours. If on standing the solution again begins to turn red, this means that precipitation of the potassium bitartrate is still continuing and it is necessary to add further reagent till the color becomes yellow. The precipitate is filtered through a paper filter and washed four times with alcohol. The filter and precipitate are then transferred back to the beaker in which the precipitation was carried out. The precipitate is dissolved in 50 ml of hot water - 80°, which on addition of NaOH becomes colored a weak rose color when phenolphthalein is used as indicator. When the potassium bitartrate is dissolved, the rose color disappears. The solution obtained, plus the filtrate, are titrated with 0.05 N NaOH to weak rose color. 1 ml 0.05 N NaOH is equivalent to 0.00195 g potassium. It is essential that the alkali used be carbonate-free. The alkali is standardized against chemically pure KCl.

The results given in Fig. 1 are those obtained for the precipitation of potassium by aniline tartrate in the presence of sodium, lithium, and magnesium, Cl', NO_3' and SO_4'', and in Table 2 results for the precipitation of potassium with pyridine tartrate in the presence of the same ions.

TABLE 1

Precipitation of Potassium by Aniline Tartrate

Taken for analysis	Amount taken, in mg	Ml of 0.5 N NaOH used	K found, in mg	Error, in %	Amounts of other salts, in mg
KCl	25.32	12.98	25.29	-0.10	
KNO_3	23.34	11.98	23.42	+0.34	
K_2SO_4	22.40	11.48	22.44	+0.18	
KCl	33.20	17.00	33.23	+0.09	200.3 NaCl
KCl	30.05	15.33	29.97	-0.27	70.2 $MgSO_4$
KCl	35.71	18.32	35.81	+0.28	89.5 LiCl

TABLE 2

Precipitation of Potassium by Pyridine Tartrate

Taken for analysis	Amount taken, in mg	Ml of 0.5 N NaOH used	K found, in mg	Error, in %	Amounts of other salts, in mg
KCl	25.03	12.79	25.00	-0.12	
KNO_3	40.70	20.92	40.89	+0.47	
K_2SO_4	22.40	11.41	22.30	-0.45	
KCl	23.00	11.80	23.07	+0.30	171.3 NaCl
KCl	23.11	11.79	23.04	-0.26	50.3 $MgSO_4$
KCl	27.51	14.06	27.48	-0.11	40.2 LiCl

SUMMARY

1. A volumetric method for the determination of potassium by precipitation

with aniline or pyridine tartrate, respectively, has been developed.

2. The presence of sodium, lithium, magnesium, chlorine, sulfate and nitrate does not interfere.

3. For simplicity and for comparative accuracy of results, the bitartrate method is to be preferred to other methods.

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THE USE OF A COBALT CATALYST FOR THE DETERMINATION OF MANGANESE BY THE PERSULFATE METHOD

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The most widely used method for the routine analysis of manganese in various materials is that in which the manganese is first oxidized to the permanganate ion - MnO_4^-, which is then determined either colorimetrically or volumetrically. This method is universally employed and a description of it is given in many text books on analytical chemistry.

Manganese can be oxidized to the MnO_4^- ion by means of periodate, sodium bismuthate, and other strong oxidizing agents. In so far as availability is concerned, and for other reasons, the only suitable oxidizing agents in practice for large number of analyses are the persulfates, which are constantly used for this purpose.

Unfortunately, the persulfates on their own cannot oxidize the lower valency states of manganese to MnO_4^- unless silver compounds, which act as catalysts, are introduced into the solution. In order to cut down on the use of the expensive and difficultly-available silver compound, a number of methods have been described which are reported to be suitable for the oxidation of manganese, and in which only very small amounts of silver have been used [1], or silver is not employed at all [2].

Practical tests, however, showed that these methods are very unreliable in many cases, so that they have not been widely accepted in practice.

Experiments which we have carried out have shown that, for the oxidation of manganese by persulfate, it is not only silver compounds which can act as catalysts.

Cobalt compounds are very good catalysts; copper and iron compounds are not so good. This fact explains why in certain instances manganese can be oxidized even in the presence of only small amounts of silver, or sometimes even in the complete absence of silver. Oxidation occurs in these cases because the substances accidentally contain a fortuitous combination of elements which act catalytically. For other substances, however, in which the composition is different, the variants of the persulfate method suggested, in which insufficient silver is used, give completely unreliable results. The catalytic action of cobalt compounds which the authors have found is completely reliable, and enables silver compounds to be replaced in the analytical determination of manganese by the persulfate method

Cobalt Compounds As Catalysts

The oxidation of persulfates has some characteristics which will be described by the authors in detail elsewhere.

Persulfates - containing the anion $S_2O_8^{2-}$ which acts as the oxidizer - can rapidly oxidize cations, but they react only slowly with like-charged anions. Quadrivalent manganese, and even more so manganese in the higher valency states, under the experimental conditions is present in solution as the anion, and it is

therefore not oxidized directly by the persulfates with sufficient rapidity. In order to achieve a rapid rate of reaction the presence of catalysts which form cations producing a strong oxidizing action is essential. The role of the catalyst thus reduces to that of an intermediate between the persulfates and the compounds of manganese being oxidized. In the case considered, therefore, the role of catalyst can be fulfilled by any element which gives rise to cations which in the lower valency states are capable of being easily oxidized by persulfates, and in the higher valency states act as strong oxidizing agents. Silver and also cobalt are suitable elements, as is apparent from the normal oxidation - reduction potential of the respective systems.

The capacity of trivalent cobalt compounds of exhibiting strong oxidizing action is well known. This is noted in analytical text books [3] and elsewhere. The reversible changes of cobalt between its different valency states occur so rapidly that a number of cobalt compounds can function as oxygen carriers, e.g., just like hemoglobin [4].

EXPERIMENTAL WORK

In the experimental work the catalytic action of cobalt was compared with that of silver, and the results obtained compared with those obtained in the absence of a catalyst. The experiments were carried out under conditions similar to those employed for the determination of manganese by the silver persulfate method.

Into a conical 250 ml flask were introduced respectively 0.002-0.01 g of manganese as a standard solution of manganese sulfate containing 0.3 mg/ml of Mn, and 15 ml of an acid mixture [600 ml dilute H_2SO_4 (1:5), 250 ml of HNO_3, sp. gr. 1.4, and 125 ml of phosphoric acid, sp. gr. 1.7]. Cobalt, iron, and the other elements or ingredients whose effect it is required to study are then added in the form of their respective solutions, and the volume finally made up to 130-150 ml with water. After the mixture has been heated to boiling, 20 ml of a 25% solution of ammonium persulfate (or 5 g of potassium persulfate) is added, after which the mixture is boiled for another two minutes. It is then cooled and after the addition of 10 ml of dilute (1:3) H_2SO_4, the permanganate formed is titrated as usual with nitrite - arsenite mixture, without the addition of NaCl. The results obtained during an investigation of the catalytic action of various elements are given in Table 1.

TABLE 1

The Catalytic Action of Various Elements

For the oxidation of Mn^{II} with ammonium persulfate in 150 ml of solution containing 5.0 mg of Mn, 0.1 mg of catalyst (calculated on the element), 15 ml of acid mixture, and 20 ml of 25% ammonium persulfate were added. The mixture was boiled for 2 minutes.

No. of expt.	Catalyst	% Mn^{II} oxidized to MnO_4^-
1	No catalyst	0
2	Ag ($AgNO_3$)	98.3
3	Co ($CoSO_4$)	100.0
4	Cu ($CuSO_4$)	60.0
5	Fe [$Fe_2(SO_4)_3$]	73.0
6	Hg ($HgCl$)($HgCl_2$)	0
7	Ni ($NiSO_4$)	0
8	Ce [$Ce_2(SO_4)_3$]	0
9	V $V_2O_2(SO_4)_2$	0
10	Mo [$(NH_4)_2MoO_4 \cdot 4MoO_3 \cdot H_2O$]	0
11	Bi $Bi(NO_3)_3$	0
12	Pb [$(CH_3COO)_2Pb$]	0

The effect of vanadium and molybdenum is interesting. These elements are not catalysts themselves, but when they are present simultaneously with cobalt, the formation of permanganate is more rapid than when cobalt alone is used.

The effect of the elements which act catalytically (Ag, Co, Cu, Fe) was also studied for various manganese contents. The results obtained, which are given in Table 2, show that it is cobalt and silver which are the best catalysts for the process.

TABLE 2

Comparative Determination of Manganese in Pure Solutions Using Various Catalysts

Volume of solution 150 ml. 0.1 mg of catalyst (calc. as the element), 15 ml of acid mixture, 20 ml of 25% ammonium persulfate are added. The mixture is boiled for 1-1.5 minutes.

Mn taken, in mg	Mn found, in mg			
	Catalyst			
	Ag	Co	Cu + Fe	Cu
1.60	1.56	1.68	1.68	0.21
2.56	2.50	2.45	2.05	1.52
3.20	3.25	3.30	2.82	2.20
4.16	4.14	4.14	4.09	-
4.80	4.77	4.60	3.18	-
6.40	6.40	6.40	-	-

Results are given in Table 3 which illustrate the effect of the presence of various elements often present in steels and cast iron on the reaction. In these cases the manganese was determined in the presence of 1 g iron, introduced into the solution as ferrous sulfate.

TABLE 3

Effect of Various Elements on the Determination of Manganese by the Cobalt-Persulfate Method

Volume of solution 150 ml. To the solution were added 1 g iron and the test element, 15 ml of the acid mixture, 3.2 mg Mn, 10 ml of 0.5% $CoSO_4 \cdot 7H_2O$ solution, and 15 ml of 25% ammonium sulfate solution. The solution was heated for 1-1.5 minutes at the boiling point.

No of expt.	Amount of element added (calcd. on the element)	Manganese	
		Amount taken, in mg	Amount found, in mg
1	None	3.2	3.19; 3.20
2	Si 5.0 mg	3.2	3.29
3	P 0.6 mg	3.2	3.29; 3.20
4	Cr 8.8 mg	3.2	3.25
5	V 1.0	3.2	3.19; 3.15
6	Mo 4.8	3.2	3.20
7	Ti 0.14	3.2	3.29
8	Ti 1.4	3.2	2.38
8-a	Ti 1.4	3.2	3.20[1]
8-b	Ti 4.2	3.2	1.5; 0.82
9	Ti 1.4 + Mo 4.8	3.2	1.14
10	Ti 1.4 + V 1.0	3.2	3.15

[1] 2 ml of $CoSO_4$ taken

From the results adduced in Table 3 it is clear that the effect of titanium is noteworthy. Under the experimental conditions, titanium apparently somehow links up with part of the cobalt (or does not succeed in oxidizing the Mn^{IV}, as a result of which all the manganese present is not oxidized to MnO_4^-. If, however, a large amount of cobalt is taken, the oxidation of the manganese proceeds normally (Table 3, experiment 8-a). In the presence of a combination of elements which accelerate the oxidation process, of perhaps paralyze the capacity of the titanium to link up with cobalt (e.g., a combination such as Ti + V), the manganese is normally oxidized even when the amount of cobalt is not increased. We also observed that a large amount of titanium hinders the determination of manganese by the usual silver - persulfate method. In order to oxidize Mn^{II} to MnO_4^- successfully, it is essential that the acidity of the solution be at a definite level, and the acid of a definite composition. This holds good to practically the same extent whether it is silver or cobalt that is used. When sulfuric acid was used alone, normal oxidation of Mn^{II} to MnO_4^-, using cobalt as a catalyst, was observed only in solutions containing not less than 10 ml of concentrated H_2SO_4 in 100 ml of the oxidizing solution. When only phosphoric acid was used, good oxidation results were not obtained, even for a phosphoric acid content of 15 ml H_3PO_4, sp.gr. 1.7, per 100 ml solution. When a mixture of H_2SO_4 and H_3PO_4 is used, it is possible to get good results over a wide acidity range. For a content of 0.7-7% H_3PO_4 (by volume for acid of sp.gr. 1.7), the concentration of H_2SO_4 can be varied between 1.5 and 3% (by volume). If the concentration of H_3PO_4 does not exceed 5% (by volume), then it is possible to use H_2SO_4 at 5% (by volume). A change in concentration of cobalt within the limits 0.7-7 ml of 0.5% $CoSO_4 \cdot 7H_2O$ / 100 ml, and possibly over an even wider range, does not affect the results.

TABLE 4

Determination of Manganese in Standary Alloys by the Cobalt-Persulfate Method

No. of expt.	Alloy	Mn content of alloy, in %	Mn determined, %			
			Catalyst			No catalyst
			Co	Co+Ni	Co+Cu	
1	Cast iron 17-c	1.57	1.60		1.62	-
2	Cast iron 63	2.41	2.40	2.44	-	-
3	Steel 20 G	0.66	0.67	0.63	0.65	-
4	Steel 118-a	0.46	0.46	0.47	0.44	-
5	Steel 150	0.83	0.83	0.80	0.81	-
6	Steel 86-a	0.48	0.50	0.49	-	-
7	Bronze 68-a	1.49	-	1.49	-	-
	Aluminum alloys					
8	Normal 69-a	0.61	0.60	0.61	0.61	-
9	Normal 72	0.33	0.35	0.35	0.33	0.30
10	Normal 74	0.22	0.23; 0.24	0.23	-	0.18
11	Normal 75	0.60	0.59	0.60	0.59, 0.60	0.43
12	Normal 76	1.00	0.99; 1.03	0.95	0.99	0.38
13	Normal 78	0.68	0.69; 0.65	1.05	0.67	
			0.70	-	0.68	0.28
	Aluminum alloys containing Ni and Ti (up to 0.5%)					
14	Alloy No. 21	0.44	0.45	-	-	-
15	Alloy No. 24	0.43	0.44	-	-	-
16	Alloy No. 25	0.41	0.40	-	-	-

Since cobalt compounds are readily available and difficulties crop up when certain other elements, such as titanium, are present, low concentrations of cobalt must be avoided. This is possible because for analytical purposes relatively expensive cobalt salts of high purity are not essential. Technical cobalt salts which contain Ni and Fe are completely satisfactory; of course the salts must be checked for the absence of manganese. The presence of Ni salts is even beneficial, since the green color of the nickel salts is supplementary to the rose color of the cobalt salts, and a solution containing both cobalt and nickel in the ratio 1:3 (calculated on the metals) generally appears colorless.

As indicated at the beginning of the article, in some cases when catalytically active elements are fortuitously present in the test object, manganese can be oxidized by persulfate even without the addition of a special catalyst. Naturally, results obtained in the absence of catalysts cannot be regarded as reliable.

Results for the determination of manganese in standard samples ("normals") by the procedure outlined below are given in Table 4, together with results for some of the salts when no catalyst was used.

From these results it is clear how unreliable determinations without a catalyst are.

Determination of Manganese by the Cobalt Persulfate Method

The method is applicable in those cases where the silver-persulfate can be used. Catalysts 1, 1a, and 1b act in the same way, but mixed catalysts are more convenient because they do not possess the rose color which is characteristic of solutions of cobalt salts

Reagents Required

1) Cobalt catalyst: 0.5% solution of $CoSO_4 \cdot 7H_2O$ in water[1].

1a) Cobalt-copper catalyst: an aqueous solution containing 0.5% $CoSO_4 \cdot 7H_2O$, and 2% $CuSO_4 \cdot 5H_2O$.

1b) Cobalt-nickel catalyst: aqueous solution containing 0.5% $CoSO_4 \cdot 7H_2O$, and 1.5% $NiSO_4 \cdot 7H_2O$.

2) Acid mixture: to 600 ml of dilute H_2SO_4 (1:5) is added 250 ml HNO_3, sp. gr. 1.20, and 125 ml phosphoric acid, sp. gr. 1.7. Nitric acid, sp. gr. 1.4, is used for preparing the acid mixture for copper and aluminum alloys.

3) Ammonium persulfate – 25% solution.

4) H_2SO_4 – dilute, 1:3.

5) Standard solution of arsenite-nitrite mixture. It is standardized against a standard alloy by the method described below. Titrations can be made with either sodium arsenite or sodium thiosulfate.

Analytical Procedure

The test sample, which preferably does not contain more than 0.01 g of manganese, is dissolved in 25 ml of the acid mixture. When solution is complete, oxides of nitrogen are expelled by boiling, after which the solution is diluted with water to 150 ml. Ten ml of the catalyst solution is added and the mixture heated to boiling. 25 ml of the persulfate solution is then added carefully to the boiling solution and the whole boiled up again and the boiling maintained for 1-2 minutes, after which it is stood in a warm place until all the persulfate has decomposed. The solution is cooled in running water, and after

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1) Technical cobalt salts which have been checked for the absence of manganese can be used for the preparation of the cobalt catalyst, as well as cobalt compounds extracted from residues obtained during the determination of cobalt by the nitroso- β -naphthol method, electrolytically, or by other methods.

addition of 10 ml of (1:3) H_2SO_4, it is titrated with the arsenite-nitrite mixture without addition of NaCl as is usually done when working with silver catalysts.

SUMMARY

Cobalt can be used as a catalyst instead of silver for the oxidation of manganese by ammonium or potassium persulfate to permanganate, which is subsequently determined colorimetrically or volumetrically.

The procedure for carrying out the oxidation and the method of determining the permanganate thus formed remains the same as when silver is used.

In view of the small amount of cobalt salt added, especially if it is added in admixture with nickel or copper, the test solution does not have the usual rose color associated with solutions of cobalt salts.

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THE DETERMINATION OF PRIMARY ALCOHOLS

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The method of estimating alcohols by acetylation with pyridine solutions of acetic anhydride has been known for a long time [1]. This method is based on the acetylation of an aliquot of the test alcohol with an accurately measured – volume or weight – amount of the acetylating agent, with subsequent determination of the excess acetic anhydride by titration.

The study which we made of this method for the determination of alcohols showed that by introducing a number of changes it is possible to increase its accuracy for primary alcohols, and to make it suitable for the determination of low molecular weight alcohols and their aqueous solutions, and also to simplify the analytical procedure.

Primary alcohols can be quantitatively acetylated in one hour at room temperature, so that the usual heating is unnecessary. This fact enables the acetylating method to be used for the determination of volatile alcohols and mixtures containing water. The accuracy of the determination depends on the accuracy with which the acetylating mixture can be measured out. For this purpose it is most convenient to use a pipet provided with a two-way tap.

During the study of the possibility of acetylating in the cold, we discovered some peculiarities in the behavior of individual alcohols. Methyl alcohol is acetylated quantitatively in 5-10 minutes; the excess acetic anhydride does not play any role. Of all the primary alcohols tested, ethyl alcohol was the most difficult to acetylate. When ethyl alcohol is being determined it is essential that the amount of acid used up in forming the ester should not be greater than 25% of the total amount. For aqueous alcohol solutions, a two-hour acetylation period is necessary; phenols are acetylated quantitatively, but also require a greater reaction time (2 hours). Primary alcohols having a double bond in the 2,3-position are acetylated at a slower rate than the saturated alcohols, so that 2 hours is also necessary for them to react completely. Secondary alcohols in pyridine at room temperature are not fully acetylated. Tertiary alcohols in general do not react, therefore the presence of tertiary alcohols does not interfere with the determination of primary alcohols.

Results for the determination of primary alcohols are given in Table 1, and for aqueous alcoholic solutions in Table 2.

EXPERIMENTAL

To an aliquot of the test alcohol weighing 0.005-0.008 mole, contained in a flask fitted with a ground glass stopper, is added, by means of a pipet with a two way tap, 3-4 ml of the acetylating mixture. The acetylating mixture is prepared by mixing one part of acetic anhydride with three parts of pyridine. After standing for one hour (or two hours for unsaturated alcohols and phenols), 20 ml of hot water is added to the contents of the flask and, after cooling, 20-25 ml of 0.5 N alkali added by means of a pipet, in order to neutralize the bulk

of the acid. The rest of the acid is then titrated against the 0.5 N alkali in a buret, using phenolphthalein as an indicator.

TABLE 1

Results for the Determination of Primary Alcohols

No.	Alcohol	Found, % of that originally taken	No.	Alcohol	Found, % of that originally taken
1	Methyl alcohol	100.2	10	Octyl alcohol	99.35
2	Methyl alcohol	99.15	11	Benzyl alcohol	100.00
3	Ethyl alcohol	100.1	12	Phenylethyl alcohol	100.2
4	Ethyl alcohol	100.7	13	" "	99.97
5	Propyl alcohol	100.1	14	Cinnamic alcohol	99.2
6	Propyl alcohol	98.8	15	" "	98.8
7	Isobutyl alcohol	100.3	16	Geraniol	98.1
8	Isobutyl alcohol	100.0	17	Decanediol	98.9
9	Isoamyl alcohol (Fermentation)	98.8			

TABLE 2

Results for the Analyses of Aqueous Alcoholic Mixtures

No.	Alcohol used	Concentration, in %	
		Taken	Found
1	Methyl alcohol	50.8	51.3
2	Ethyl alcohol	18.0	18.3
3	Ethyl alcohol	49.9	49.4
4	Propyl alcohol	20.2	21.2
5	Propyl alcohol	49.9	50.9

A blank is done in exactly the same way. The differences in the titres gives the amount of alcohol present; 1 ml of 0.5 N alkali is equivalent to 0.5 millimole of alcohol.

If a volatile alcohol or mixtures containing volatile components are to be analyzed, e.g., the determination of an alcohol in ethyl acetate or chloroform, then they are introduced into a weighed, stoppered flask already containing the acetylating mixture. When mixtures containing aldehydes are titrated, the rose color tends to fade. Titration must be carried out until a stable red color is obtained.

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CRITICISM

A.A.Cherepenikov.' "Handbook on the Testing and Analysis of Natural Gas", Moscow, State Geol. Press, 1951. 120 pages, 5000 copies, Price 7 rubles, 10 kopecks.

The study of natural gas is becoming of ever increasing practical importance as a result of the exceptionally rapid development of a number of branches of the national economy. Serious attention was given to the development of the gas industry in the directives of the XIX Congress of the Communist Party of the Soviet Union.

In the light of these decisions, the preparation of new cadres of gas operators, the further development of gas analysis, and the introduction into the most diverse branches of industry of basic methods for testing and analyzing gases, have become practically acute problems.

Hitherto the number of textbooks which collect together all the testing methods for gases, and can be of help to various specialists interested in this branch of knowledge has been completely insufficient. From this point of view therefore we must welcome the appearance of "Handbook on the Testing and Analysis of Natural Gas", which has been written by A.A. Cherepenikov, who can truly be considered as one of the oldest and most experienced investigators of natural gas in the Soviet Union. A large number of original articles have come from his pen in which methods for the determination of individual gases, and the natural gas resources of various regions in the USSR, have been described.

The questions dealt with in this book transcend the limits of interests of "chemists and testers working on the study of natural gas", as the author himself points out in his introduction, and should interest a wider circle of readers than A.A.Cherepenikov intends. Thus, this book will undoubtedly get attention from workers in various branches of science and practice.

The demands on books of this kind with respect to completeness are particularly high; in addition they must be completely up to date with respect to contemporary methods and techniques of gas analysis.

Unfortunately, the textbooks which have been published on this subject suffer from a number of defects which considerably lower their practical value. In this connection A.A.Cherepenikov's book is no exception.

In discussing the book's drawbacks we must first of all point out that it is not full enough. Thus, in the chapter on "Methods of Testing Natural Gas", in observing that it is essential to sweep out the apparatus with gas, the author does not indicate how much gas should be used for this purpose; and when describing the necessity of heating vessels when producing a vacuum, he does not say for how long, or at what temperature. We consider that in a textbook designed to serve as a reference book, it is not permissible to write: "a tube of the respective diameter" (p. 16); "the smallest possible internal diameter" (p. 17) etc.. Similarily, in a handbook it is not usual just to mention the principle underlying some particular technique or method, as the author does in the case of an apparatus for hermetically sealing the mouth of the bore hole designed by M.N.Vorobev (p. 8), or in his description of a method of opening and sealing up vessels with "spark" gas (p. 21), and in many other places throughout the book. The description of such important apparatus as samplers

should not be substituted by references to the authors' names without any indications of the literature (p. 13, et al), which incidentally appears only very seldom in the bibliography at the present time.

In the section dealing with the documentation of tests the author confines himself to listing the questions of registration cards when he should bring forward the typed form of card.

The section "Methods of Chemical Analysis of Natural Gas" also contains a number of general and indefinite instructions. E.g., "the method for the determination of H_2S by absorption in a solution of cadmium acetate and chloride, with subsequent decomposition of the cadmium sulfide formed with HCl, and iodometric titration of the H_2S evolved" p. 37, is given without a description of the apparatus, preparation of reagents, or the necessary calculations. It is well known that the preparation of baryta water for the absorption of a small amount of CO_2 is quite complex. The author (p. 8) has only this to say "all precautions should be taken to prevent the solution from coming into contact with the atmosphere". It is obvious that such instructions are not enough for the preparation of the solution. The same can be said about the preparation of palladium black (p. 6), the removal of kerosene from metallic calcium (p. 92), and the preparation of pentane baths (p. 83), etc..

There are no indications how to determine the density or the calorific value of natural gas.

Similar inaccuracies occur in many places throughout the book. The reader is compelled to look for definite answers to the practical questions brought up in A.A.Cherepenikov's book in other textbooks on various branches of knowledge. The author does not come to the reader's help in his search - there are no bibliographical references. An understanding of many of the questions relating to the apparatus is rendered difficult by the absence of the requisite diagrams and sketches. (pp. 111, 112 etc.).

The greatest drawback is the absence of a description of a large number of methods for testing and analyzing gases, which are widely used in practice but are not used by the author himself in his particular work. By confining himself to giving descriptions of only the work and apparatus used in his own laboratory, A.A.Cherepenikov in our opinion has made his book poorer than it need be. This is particularly evident in the sections dealing with the determination of individual hydrocarbons, micro and semi-micro gas analysis, and the determination of the inert gases.

Other factors which lower the practical value of the book are the smallness of the chapter devoted to "Some practical hints", and the absence of a number of essential reference tables. The material in this part of the book is completely inadequate and is of a rather haphazard character.

The experience of publishing A.A.Cherepenikov's book and also of other similar books shows that bringing out a really good handbook which gives a complete coverage of all the fundamental questions of gas technology is a particularly difficult task, and in our opinion is a problem which can only be satisfactorily solved by collaboration of a number of authors.

The obvious necessity of publishing such a book on gas analysis impels us to draw the attention of Scientific Societies to the problem of compilation and publication of such a book.

M.G.Gurevich and K.P.Florensky

November 12, 1952.

NEW REAGENTS

WATER SOLUBLE SULFONPHTHALEIN INDICATORS

New water-soluble sulfonphthalein indicators have been proposed by the Institute of Chemical Reagents for the colorimetric determination of pH.

These soluble indicators change their color for the same pH changes as the usual sulfonphthalein indicators.

No alcohol or standard alkali is necessary for the preparation of their solutions. The indicator solution is prepared by dissolving 0.1 g of the solid water soluble sulfonphthalein in 100-250 ml of distilled water.

The advantagesof these water-soluble indicators as compared to the ordinary type are obvious.

"Glavkhimreaktiv" issue the following water soluble indicators:

	pH
Thymol Blue	1.2-2.8 8.0-9.6
Bromphenol Blue	3.0-4.6
Bromcresol Purple	5.2-6.8
Bromthymol Blue	6.0-7.6
Penol Red	6.4-8.2
Cresol Red and others	7.0-8.6